

PARVENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

Date of mailing (day/month/year)	ETATS-UNIS D'AMERIQUE in its capacity as elected Office
01 November 2000 (01.11.00)	
International application No. PCT/US00/02445	Applicant's or agent's file reference BSAT00-01PCT
International filing date (day/month/year)	Priority date (day/month/year)
31 January 2000 (31.01.00)	01 February 1999 (01.02.99)
Applicant	
POPE, John et al	

1. The designated Office is hereby notified of its election made:

in the demand filed with the International Preliminary Examining Authority on:

30 August 2000 (30.08.00)

in a notice effecting later election filed with the International Bureau on:

2. The election was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer G. Bähr</p> <p>Telephone No.: (41-22) 338.83.38</p>
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 15 JUN 2001

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Applicant's or agent's file reference BSAT00-01PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/02445	International filing date (day/month/year) 31 January 2000 (31.01.2000)	Priority date (day/month/year) 01 February 1999 (01.02.1999)
International Patent Classification (IPC) or national classification and IPC IPC(7): H01M 4/60 and US Cl.: 429/213		
Applicant BLUE SKY BATTERIES		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of **4** sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of **0** sheets.

3. This report contains indications relating to the following items:

- I Basis of the report
- II Priority
- III Non-establishment of report with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 30 August 2000	Date of completion of this report 01 June 2001 (01.06.2001)
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Carol Chaney  Telephone No. 703-308-0661

I. Basis of the report

1. With regard to the elements of the international application:*

 the international application as originally filed. the description:

pages 1-33 as originally filed

pages NONE, filed with the demandpages NONE, filed with the letter of _____ the claims:

pages 34-39, as originally filed

pages NONE, as amended (together with any statement) under Article 19pages NONE, filed with the demandpages NONE, filed with the letter of _____ the drawings:

pages 1-6, as originally filed

pages NONE, filed with the demandpages NONE, filed with the letter of _____ the sequence listing part of the description:pages NONE, as originally filedpages NONE, filed with the demandpages NONE, filed with the letter of _____

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item. These elements were available or furnished to this Authority in the following language _____ which is:

 the language of a translation furnished for the purposes of international search (under Rule 23.1(b)). the language of publication of the international application (under Rule 48.3(b)). the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

 contained in the international application in printed form. filed together with the international application in computer readable form. furnished subsequently to this Authority in written form. furnished subsequently to this Authority in computer readable form. The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished. The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.4. The amendments have resulted in the cancellation of: the description, pages NONE the claims, Nos. NONE the drawings, sheets/fig NONE5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

V. Reasoned statement under Art. 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. STATEMENT**

Novelty (N)

Claims 1-4 and 25-26 YES
Claims 5-24 NO

Inventive Step (IS)

Claims 25-26 YES
Claims 1-24 NO

Industrial Applicability (IA)

Claims 1-26 YES
Claims none NO**2. CITATIONS AND EXPLANATIONS (Rule 70.7)**

Claims 5-24 lack novelty under PCT Article 33(2) as being anticipated by Maxfield et al., US Patent 4,472,488.

Applicants' claims are directed to a battery cathode material comprising an electronically conductive polymer with covalently-bonded sulfur moieties. Maxfield et al. disclose a cathode material which is the product of a conjugated-backbone polymer and cyclic sulfur compounds, including thiophenes. The product would contain sulfur groups covalently bonded to the conjugated polymer. (Note column 4, lines 47-54.)

Claims 1-4 lack an inventive step under PCT Article 33(3) as being obvious over Maxfield et al. Applicants' claims are directed to a method of choosing a cathode material. Although Maxfield et al. do not explicitly teach a method for choosing a cathode material, it is clear that characteristics such as low cell resistance, stability against decomposition in electrolyte, and high charge capacity are significant in choosing cathode materials. (Note col. 3, lines 41-54.) Maxwell's discussion of the importance of these parameters would motivate one of ordinary skill to choose a cathode material based upon applicants' recited factors.

Claims 25 and 26 meet the criteria set out in PCT Article 33(2)-(4), because the prior art does not teach or fairly suggest cathode active materials with a single component sulfur-based conducting polymer as claimed by the applicants.

----- NEW CITATIONS -----
NONE

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the questions whether the claims are fully supported by the description, are made:

Claim objected to as lacking clarity under PCT Rule 66.2(a)(v) because practice of the claimed invention is not adequately described in writing, as required under PCT Rule 5.1(a)(iii), for the reasons set forth in the immediately preceding paragraph.

Claims 1-26 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claims are indefinite for the following reason(s):

The terms "ease of fabrication using straightforward synthetic procedures"; "high density of electroactive species", "good overlap of thermodynamic potentials" and "many repeated charge and discharge cycles" and "suitable fade characteristic" are relative terms, and are thus unclear. The specification fails to define "ease", "straightforward", "high", "good overlap", "many" and suitable.

In claims 9-26, the term "single component sulfur-based conducting polymer" lacks clarity because it is unclear whether "single component" modifies "sulfur-based" or "polymer" and the meanings of "sulfur-based" and "component" are not defined.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: SINGLE COMPONENT SULFUR-BASED CATHODES FOR LITHIUM AND LITHIUM-ION BATTERIES

(57) Abstract

The present invention pertains to the selection of cathode materials. The cathode materials of concern are the conducting polymer or backbone and the redox active species or sulfur species. The selection of the materials is based on the characteristics of the materials relating to the other components of the batteries and to each other. The present invention also pertains to the resultant cathode materials, particularly a selected cathode material of a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer, and most particularly a thiophene based polymer with covalently linked sulfur species. The conducting polymers have been covalently-derivatized with sulfides and/or sulfide-containing groups as battery cathode materials. The present invention also pertains to a battery employing the selection method and resultant cathode materials.

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SINGLE COMPONENT SULFUR-BASED CATHODES FOR LITHIUM AND LITHIUM-ION BATTERIES

RELATED APPLICATIONS

This application claims priority to U.S. Provisional patent application 60/118,068, the contents of which are incorporated herein by reference in their entirety.

TECHNICAL FIELD

The present invention relates generally to cathodes for rechargeable batteries. More particularly, the present invention relates to cathode materials based on conducting polymers and sulfur or selenide species and the method of selecting conducting polymers and sulfur or selenide species. The selection method accounts for characteristics of the conducting polymer and the sulfur or selenide species and the specific capacity, capacity fade, charge and discharge rate, physical and chemical stability, safety and other characteristics associated with battery cycles. More particularly, the present invention relates to a single component sulfur-based conducting polymer for use in lithium batteries and the synthesis of such material.

BACKGROUND

Increasing reliance on sophisticated electronic technologies has exacerbated a need for reliable, portable sources of energy. The current worldwide market for rechargeable batteries exceeds \$4 billion. However, an estimated \$6 billion market in the United States alone remains untapped due to the inability of available products to meet the needs of a large industrial, consumer, and military based market. And the need is growing, particularly for high power applications such as electric vehicles and load-leveling equipment and weight or volume constrained applications such as portable computers, cellular phones, etc. Creative alternatives to current battery technologies must be developed.

Among available technologies, lithium and lithium-ion batteries represent the most promising technologies, especially in terms of their attractive energy densities when compared to nickel cadmium and nickel-metal hydride cells. This promise can be attributed in large part to the extremely high specific capacity available in theory from lithium (3862 A h/kg) and the reasonable charge capacity available from lithium-intercalated carbon (e.g. for LiC_6 , 372 A h/kg) anodes.

However, realization of the full potential of that technology has been awaiting development of 1) electrolyte compositions able to withstand the high reactivities of those

anodes, and 2) inexpensive, stable cathodic materials also able to store high charge capacities. The present invention addresses resolution of the latter issue.

Batteries currently marketed utilize LiCoO₂ cathodes, a material that has a theoretical specific capacity of 274 A h/kg and a practical specific capacity of 100 to 150 A h/kg. In realistic terms, then, cells using LiCoO₂ can utilize only one-thirtieth of the potential energy per gram stored in lithium metal (or only one-third of the potential energy per gram stored in LiC₆). While batteries based on such cathodes are suitable to meet short-term commercial needs, significant progress in this area must be based around developing cathodes with specific capacities similar to those of the best available anodes.

In terms of alternative cathode materials being currently studied, sulfur and sulfur-containing compounds offer the best opportunities in terms of high theoretical specific capacities. Sulfur cathodes operate by storing energy as disulfide bridges, a very stable oxidized material, then releasing it by reducing to thiolate moieties. This process is illustrated in Figure 1 for one material. While sulfur cathodes were the first employed for lithium laboratory cells, their use in practical batteries was abandoned primarily due to the insulating nature of those materials, which necessitates using high temperatures in order to facilitate mass transport within the cathodes.

However, advances in understanding and controlling electronic conductivity in composite materials has signaled a revival of that class of materials, as evidenced by ongoing exploratory or commercial efforts. Experimental lithium metal and lithium ion anode

prototypes of systems recently developed match or exceed current room temperature secondary battery performances in terms of gravimetric energy density (energy delivered per mass of the cathode material).

In U.S. Patent No. 5,789,108, Chu is pursuing technology based on cathodes composed of inorganic sulfur mixed with poly(ethylene oxide) (PEO), lithium salts, and carbon powders, while Skotheim et al., in U.S. Patent No. 5,529,860, are developing cathodes based on inorganic sulfur and poly(acetylene) derivatives. Those formulations represent attempts at achieving electronic and ionic access to the sulfur in those cathode *via* dispersion in an ionically conducting medium (PEO) which contains an electronic conductor (carbon)(Chu) or the use of a conducting polymer to effect both goals (Skotheim et al.).

Although such materials show excellent specific capacities during initial cycles, neither Chu nor Skotheim et al. have commercialized a sulfur or organosulfur based secondary battery due to high capacity loss, or "fade," observed for their cells over multiple charge and discharge cycles. Consideration of the possible origins of that behavior are obscured by a general lack of knowledge regarding the complicated electrochemistry of inorganic sulfur, compounded by the varying solubilities and chemical activities of the different forms of sulfur (e.g. polysulfide, oligosulfide, dimer, monomer (S^{2-})), possible reaction between those species and the anode, and the likely growth of heterogeneous zones of non-conductive material that separate from the initial cathode mixture.

However, it is clear from recent work that the capacity fade observed is due in large part to diffusion of monomeric sulfur species out of the cathode. While interesting redox chemistry is typically evident in the first few cycles, it typically fades after several cycles to leave less desirable redox activity – *viz.* the organosulfur or sulfur or selenide component exits the cathode *via* dissolution into the electrolyte film, resulting in capacity loss during cycling.

In WO 99/03162, Skotheim et al., describe a polymer film that protects the lithium anode in a secondary battery. The film interferes to some degree with the reactions and thus reduces the overall efficiency of the battery. The film is needed when sulfur species are mobile and may migrate to the anode. Skotheim et al. do not suggest decreasing or eliminating the mobility of reactive sulfur species so that interference at the anode is decreased and thereby the efficiency of the battery is increased.

Definitions

Conducting polymer:

Conducting polymers are polymers through which electrons can move from one end of the polymer to the other. A conducting polymer transports voltage and/or current along its backbone or between its chains by changing the distribution of electrons in the polymer

chain. Such conduction typically occurs through conjugated π electronic functionalities, although some conducting polymers include other types of electronic functionalities. In some instances, conductivity occurs in short chains of the polymer ("oligomers"). In some cases, conductivity occurs in long chains of the polymer. Non-limiting examples of conducting polymers include poly(acetylene), poly(aniline), poly(pyrrole), poly(thiophene), poly(*p*-phenylene), (poly)phthalocyanine, etc. and derivatives thereof.

Redox species:

A redox species is an atom, molecule, or macromolecule that accepts or releases one or more electrons when placed under an electric field of appropriate direction and magnitude. Non-limiting examples of redox species include ruthenium hexamine chloride, ferrocene, gold, poly(pyrrole), hexanethiol, and similar species and derivatives.

Battery:

A battery is comprised of one or more cells each comprised of an electropositive anode such as lithium or nickel, an electronegative cathode such as metal oxide, sulfur, or cadmium, and an ionically-conducting separator, such as poly(ethylene oxide), propylene carbonate, or Nafion, that contain an electrolytic salt such as lithium hexafluorophosphate, sodium chloride, etc. A cell "discharges" by allowing electrons to pass via an external circuit

from a higher energy state in the anode to a lower energy state in the cathode while allowing ions to pass through the separator. In lithium-based cells, Li ions pass from the anode through the separator to the cathode. The electrons that pass through the external circuit may be used to perform work. In a rechargeable battery, this electron and ion movement may be reversed to some extent by applying an external current to the cell to "charge" the cell. The typical forms of batteries, and more specifically of lithium-based batteries are well known to those skilled in the art.

Sulfur species:

In this document, sulfur species include atoms, molecules, and macromolecules that contain at least one sulfur atom. Typical terms used to describe such molecules include organosulfur, sulfur, sulfide, disulfide, thio, thiol, thiolate, mercapto, mercaptan, etc. In some cases, the sulfur species contains a negatively-charged or proton-associated sulfur atom that is covalently bound to another atom through a single bond. This type of sulfur species is capable of releasing an associated cation or proton and forming a disulfide bond with a similar atom. In other cases, the sulfur species contains sulfur atoms that are multiply bound to other atom or atoms and are not capable of forming disulfide bonds. In all cases, in this document, sulfur species refers to atoms, molecules, and macromolecules that contain at least one sulfur atom that can act in part or in whole as a redox species.

Selenium species

In this document, selenium species include atoms, molecules, and macromolecules that contain at least one selenium atom. Typical terms used to describe such molecules include selenide, selenate, diselenides, etc. In some cases, the selenide species contains a negatively-charged or proton-associated selenide atom that is covalently bound to another atom through a single bond. This type of selenide species is capable of releasing an associated cation or proton and forming a diselenide bond with a similar atom. In other cases, the selenide species contains selenide atoms that are multiply bound to other atom or atoms and are not capable of forming diselenide bonds. In all cases, in this document, selenide species refers to atoms, molecules, and macromolecules that contain at least one selenide atom that can act in part or in whole as a redox species.

SUMMARY OF INVENTION

One aspect of the present invention pertains to the selection of cathode materials. The cathode materials of concern are the conducting polymer or backbone and the redox active species or sulfur species. The selection of the materials is based on the characteristics of the materials relating to the other components of the batteries and to each other.

In one embodiment, the selection of cathode materials is based on one or more of the following characteristics of the conducting polymer and/or the sulfur or selenide species: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; no labile protons in the material; a high density of electroactive species per weight and volume (i.e. large inherent charge capacity); good overlap of the thermodynamic redox potentials of the electroactive substituents and the conducting polymer backbone; reasonable electronic conductivity of the composite; no solubility in typical electrolyte solutions; and electrochemically, physically, and chemically stable to many repeated charge and discharge cycles. In a preferred embodiment, the selection of the cathode materials is based on all of the above identified characteristics for both the conducting polymer and the sulfur or selenide species.

In one embodiment, the selection of cathode materials is based on the overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials are chosen based on the redox mediation window. The conducting polymer mediates electrons between the current collector and the sulfur or selenium species. Conducting polymers exhibit potential-dependent conductivities. When the potential is in the "double-layer" region of the conducting polymer (that is, when the conducting polymer is releasing or accepting electrons), the conductivity of the polymer is much higher than when the potential is more negative or more positive of that region. If the conducting polymer is inherently in a less-conductive state in the potential region where the sulfur or selenium species exhibits redox species behavior, mediation of electrons

between the current collector and the sulfur or selenium species is poorly effected, the material is less desirable, and the battery performance is poorer.

In a preferred embodiment, the resulting premise of the selection process of materials is that the redox active species or sulfur species that are mobile are not compatible with long-life, high-capacity batteries.

Another aspect of the present invention pertains to resultant cathode materials identified by the use of the selection process identified above.

In a preferred embodiment, the cathode materials were selected because they exhibit overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials form a redox mediation window. The conducting polymer mediates electrons between electrode(s) and the sulfur species in an effective fashion.

In a preferred embodiment, the sulfur species is NOT covalently linked to the conducting polymer backbone. An example of this system is that comprising a mixture of poly(3,4-ethylenedioxythiophene) (PEDT) and 2,5-dimercapto-1,3,4-thiadiazole, dilithium salt (Li₂DMcT). PEDT is available as an aqueous dispersion. Li₂DMcT is dissolved directly into the PEDT dispersion at high concentrations. Properly treated films cast from that mixture are used as cathode materials in lithium and lithium-ion cells. Alternately, films are

prepared by electrochemical or chemical oxidation of the PEDT monomer and Li₂DMcT from the same or different solutions in a homogeneous or layered arrangement. Li₂DMcT contains no labile protons, so its use in the cathode is attractive. PEDT has a wide potential window of conductivity, contains no labile protons, and is not proton-doped, so its use in the cathode is attractive.

One embodiment of the present invention is the cathode materials are not mobile. Specifically, the redox active species or sulfur species is not mobile. The redox active species is bound to the conducting polymer and is not able to migrate from the conducting polymer.

In a preferred embodiment, the cathode material is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer. The link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte. In this preferred embodiment, sulfur or other sulfur species apart from the covalently linked sulfur species may or may not be present. Most preferably the cathode material contains no other sulfur or sulfur species apart from the bound sulfur species.

In a preferred embodiment, the cathode material is a thiophene based polymer with covalently linked sulfur species. Such conducting polymers have been covalently-derivatized with sulfides and/or sulfide-containing groups and employed as battery cathode materials. Physical constraints of the conducting polymer and sulfide components via covalent bonds

which are present regardless of charge state of the cathode represents a novel step in the field.

Yet another aspect of the present invention pertains to a method of synthesis of the selected cathode material.

Still another aspect of the present invention pertains to batteries which comprise an anode; cathode material(s) of the present invention, as described herein; and a separator between the anode and the cathode materials

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 shows a sulfur cathode in operation by storing energy as a disulfide bridge then releasing it by reducing to thiolate moieties.

Fig. 2 shows an example of an inappropriate overlap of thermodynamic potentials between polyaniline and an organosulfur.

Fig. 3 shows a general formula of a conducting polymer of the present invention.

Fig. 4 shows a more specific formula of the present invention.

Fig. 5 shows the substituent parts of the polythiophene conducting polymer.

Fig. 6 shows two resultant conducting polymers of the present invention.

DETAILED DESCRIPTION OF INVENTION

One aspect of the present invention pertains to the selection of cathode materials. The cathode materials of concern are the conducting polymer or backbone and the redox active species or sulfur species. The selection of the materials is based on the characteristics of the materials relating to the other components of the batteries and to each other.

In one embodiment, the selection of cathode materials is based on one or more of the following characteristics of the conducting polymer and/or the sulfur species: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; no labile protons in the material; a high density of electroactive species per weight and volume; good overlap of the thermodynamic potentials of the electroactive substituents and conducting polymer backbone; reasonable electronic conductivity of the composite; no solubility in typical electrolyte solutions; and electrochemically stable to many repeated charge and discharge cycles. In a preferred embodiment, the selection of the cathode materials is based on all of the above identified characteristics for both the conducting polymer and the sulfur species.

Molecular design of innovative sulfur-based cathode materials

The chemical and physical constraints imposed on cathode materials are substantial. The specific properties required include ease of fabrication using straightforward synthetic procedures.

In sulfur-based batteries, the sulfur species and preferably the conducting polymer must be ionically conductive for Li^+ ions. The chemistry of sulfur-based batteries necessitates the requirement of the cathode materials to be ionically conductive for Li^+ ions.

A material that contains mobile redox species presents stability, capacity fade, and safety problems when used as a cathode material in a lithium or lithium-ion or lithium polymer cell. For example, 2,5-dimercapto-1,3,4-thiadiazole contains two labile protons. Use of that material as a component of a cathode material leads to transport of the labile protons via intermediate species into the electrolyte and eventually to the anode, where spontaneous electrochemical reduction by the anode creates hydrogen gas. Similar events can occur when poly(aniline), a proton-doped conducting polymer, is used as a component of a cathode material. This constraint includes the selection of conducting polymers and sulfur species that do not contain labile protons at any stage of the battery reaction.

A battery's effectiveness is attributable to the charge capacity. Selecting a sulfur species and conducting polymer with a high density of electroactive species per weight and volume (i.e. large inherent charge capacity) increases the effectiveness of the cathode and battery overall.

A battery's effectiveness is also dependent on the electronic conductivity of the cathode materials. Selecting a sulfur species and conducting polymer with an electronic conductivity above 10^{-6} S/cm, more preferably above 10^{-5} S/cm, more preferably above 10^{-4} S/cm, more preferably above 10^{-3} S/cm, and most preferably above 10^{-2} S/cm increases a battery's effectiveness.

The solubility of the sulfur species or conducting polymer in the electrolyte inhibits the efficiency of the battery. When sulfur species or other electroactive species associated with the conducting polymer are mobile in the electrolyte, the species may migrate towards the anode and a decrease in efficiency results when the species contact the anode. Over time the anode increasingly becomes contacted with species and a loss of electroactive sites may be seen on the anode. The solubility of the sulfur species also leads to collection of the active sulfur away from the conducting polymer and therefore a loss of redox species in the cathode. Thus, selecting sulfur species and conducting polymers which are not soluble in the electrolyte solution increases the efficiency of the battery and reduces the fade and poor cyclability typical of sulfur-based batteries.

The current sulfur-based batteries in use exhibit considerable fade over even 100 cycles. Many factors contribute to the fade observed in conventional sulfur-based batteries. However, by selecting the conducting polymer and sulfur species of the cathode materials that are electrochemically stable to many repeated charge and discharge cycles the fade is reduced.

Unfortunately, previous sulfur-based cathodes have not satisfied most of these requirements. However, understanding the structure-function relationships for these materials allows sufficient tailoring of their properties to increase their effectiveness in rechargeable batteries.

Redox Mediation Window

In one embodiment, the selection of cathode materials is based on the overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials are chosen based on the redox mediation window. The conducting polymer mediates electrons between electrode and sulfur species.

An example of *inappropriate* overlap of thermodynamic potentials, the redox response of composite cathode components are shown in Figure 3. While oxidation of the organosulfur occurs when the polyaniline is primarily in its metallic state (indicated by a dashed line at 3.1 V), reduction of the resulting disulfide occurs in a potential window where

the polyaniline is primarily in its insulating state (indicated by a dashed line at 2.6 V). The practical consequences of that thermodynamic mismatch between components is apparent in devices using such cathodes – charging of the cells occurs quickly, but discharging is slow and typically incomplete.

Cathode Materials

Another aspect of the present invention pertains to resultant cathode materials identified by the use of the selection process of the present invention.

In a preferred embodiment, the cathode materials were selected because they exhibit overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials form a redox mediation window. The conducting polymer mediates electrons between electrode(s) and the sulfur species.

In a preferred embodiment, the resulting premise of the selection process of materials is the redox active species or sulfur species that are mobile are not compatible with long-life, high-capacity batteries. The sulfur species in the cathode materials is not mobile and is not soluble in the electrolyte of the battery and does not include labile protons that are mobile or soluble in the electrolyte. More preferentially, the cathode materials are not mobile. Specifically, the redox active species or sulfur species is not mobile. The redox active species is bound to the conducting polymer and is not able to migrate from the conducting polymer.

In a preferred embodiment, the cathode material is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer. The link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte. In this preferred embodiment, sulfur or other sulfur species in the cathode apart from the covalently linked sulfur species may or may not be present. Most preferably the cathode material contains no other sulfur or sulfur species apart from the bound sulfur species.

In a preferred embodiment, the cathode material is a thiophene based polymer (such as polythiophene) with covalently linked sulfur species. Such conducting polymers have been covalently-derivatized with sulfides and/or sulfide-containing groups as battery cathode materials. Physical constraints of the conducting polymer and sulfide components via covalent bonds which are present regardless of charge state of the cathode represents a novel step in the field.

Using the method of the present invention a resultant cathode material was identified. Sulfur-derivatized conducting polymers based on the oxide-substituted poly(thiophene) backbone are synthesized. Those polymers show good thermodynamic overlap with sulfide oxidation and reduction (*i.e.* charge and discharge). Covalent linkage of the sulfur groups to the backbone provides molecular-level ordering of the material, effecting homogeneous conductivity, cycling stability, and physical structure of the cathode.

In one embodiment, the sulfur-derivatized conducting polymers have the general formula $(R_i)_n(Y_jA_k)_m$ where R is monomer or oligomer units of a conducting polymer, i is 1 to n and n is greater than 20, more preferably greater than 100, more preferably greater than 1000, more preferably greater than 10,000 and most preferably greater than 100,000; Y is a functionalizing group that provides additional physical or chemical properties to the conducting polymer and j is 0 to n; A is a sulfur species, k is 1 to n and m is 1 to 12. A simplified representation of the general formula is shown in figure 3.

More particularly, the sulfur-derivatized conducting polymers have the general formula $(R)_n(YS_m)_x$ where R is a conducting polymer backbone and n is greater than 20, more preferably greater than 100, more preferably greater than 1000, more preferably greater than 10,000 and most preferably greater than 100,000; Y is a functionalizing group; S is an organosulfur moiety, m is 1 to 12 and x is 1 to 4. In a preferred embodiment, R is polythiophene or its derivatives. The formula is shown in figure 4. The preferred embodiment is shown in figure 5 based on the polythiophene backbone R_n .

Specifically, the present invention also concerns covalently derivatizing an electronically conducting polymer with a high density of electroactive sulfur species. The materials operate near the high oxidation potentials exhibited by the more common metal oxide cathodes but show far better ionic conductivity. This is accomplished by applying pre-existing, high yield organic synthesis procedures to the formation of monomeric, and then polymeric species composed of thiophene-based polymer chains with thiolate substituents. The synthesis steps are geared toward forming a reasonably high molecular weight polymer

while at the same time incorporating a high density of electroactive species that are not only electrochemically stable, but also protect the polymer from chemical degradation.

Another aspect of the present invention pertains to a method of designing conducting polymers covalently-derivatized with sulfur species such that the chemical, physical, and electrochemical properties of the designed material are advantageous to use in a rechargeable cell. For example, for the conducting polymers represented by Figure 6, the number of carbon atoms between the oxygen atoms and the sulfide-containing six-membered ring are varied to affect both the proximity of the sulfide-containing six-membered ring to the conducting polymer backbone and the flexibility of the attachment of the sulfide-containing six-membered ring. Likewise, other atom or functional groups such as sulfur, selenium, amides, amines, etc. are substituted for the oxygen atoms in order to affect the conductivity and relative energy of the conducting polymer backbone. Furthermore, the number of carbon atoms in the sulfide-containing six-membered ring are reduced or increased in order to affect the electronic, physical, or chemical properties of the sulfur atoms. For instance, reducing the number of carbon atoms to produce a sulfide-containing four-membered ring causes additional strain on the disulfide oxidation product and results in higher potentials for redox activity of that sulfur species. Finally, additional substituents are placed on the conducting polymer ring, functionalizing group, or sulfur species in order to affect the chemical and physical properties of the material. For instance, attaching a alkylsulfonate at the carbon atom above the oxygen atom increases the solubility and miscibility of the material.

Yet another aspect of the present invention pertains to a method of synthesis of the selected cathode material.

Still another aspect of the present invention pertains to batteries which comprise an anode; cathode material(s) of the present invention, as described herein; and a separator between the anode and the cathode materials. A battery with the cathode material as sulfur-derivatized conducting polymers based on the oxide-substituted poly(thiophene) backbone are used as a substitute cathode in existing lithium, lithium-ion, and lithium polymer rechargeable batteries.

Synthesis of Sulfur-Derivatized Cathode Materials.

Thiophene based cathode materials

Two thiophene-based polymers, structures shown in Figure 6, were synthesized. The first (PDDT) follows a tractable route to produce a material with an attractive theoretical specific capacity (235 A h/kg). Synthesis of the second polymer (PDPT) was more uncertain due to its bulky substituents, yet its synthesis yielded a material with a very attractive theoretical specific capacity (332 A h/kg).

PDDT was chosen as a cathode material in part because a stable 6-member ring is formed during oxidation to the disulfide.

PDPT, shown in Figure 6, offers higher specific capacity because of the increased number of disulfide substituents

Development of deposition techniques for the polymers synthesized

Processing of conducting polymers is a non-trivial issue – the very traits that make those materials conductive also result in low solubility of the polymers in most solvent systems. That problem is compounded for the systems described herein by the typically poor solubility of sulfide species.

For a preferred embodiment, if a particular polymer exhibits some solubility in a given, non-protic solvent such as N-methylpyrrolidinone or methylene chloride, then a saturated solution is directly cast onto the current collector. Care was taken to generate uniformly small particle sizes of the polymer prior to deposition. Evaporation of the solvent under normal drying conditions leads to a relatively adherent film due to the soluble phase acting as a binder. If a quality film is generated, but adhesion to the current collector is poor, then the current collector is chemically or mechanically treated prior to film deposition.

For another embodiment, mechanical or high pressure or temperature methods are employed to prepare suitable films of the cathode material. For example, extrusion, heat-pressing, and other methods are available.

In a preferred embodiment, the derivatized conducting polymer is prepared by chemical or electrochemical oxidation of its monomer in the presence of a suitable current collector. For example, the monomer of PDDT (Figure 6) is electrochemically oxidized at a stainless steel electrode by applying a potential of more than one volt versus the Ag/AgCl reference redox couple. This application results in the preparation of a film of PDDT on the stainless steel suitable for use as a cathode material.

If a particular polymer is not sufficiently soluble in any appropriate solvent system, and if the mechanical preparation of reasonable films is not possible, carbon paste electrodes containing the polymers are prepared in order to allow electrochemical testing of their properties.

Example 1

The first attempted, unsuccessful, synthesis involved Cu(I) assisted nucleophilic displacement of the bromine groups of 3,4-dibromothiophene with 1,2-dithiane-4,5-diol to form the desired cyclic ester (Scheme 1).

Experimental:

3,4-(1,2-dithiane-4,5-diol) Thiophene. Pyridine (5 mL) was added to 1,2-dithiane-4,5-diol (0.27 g, 1.80 mmol), CuI (0.01 g, 0.07 mmol) and KO'Bu (0.06 g, 0.54 mmol) to produce a yellow solution which turned green after stirring at ambient temperature over a period of 1h. 3,4-dibromothiophene (0.09 g, 0.36 mmol) was then added to the reaction mixture which was heated at 100 °C for 24h. A distillation was then done to remove pyridine. The remaining solution was dissolved in 0.05 M EDTA to remove complexed copper. An extraction was done with ethyl acetate. The organic, ethyl acetate, layer was concentrated under vacuum. This procedure did NOT result in the desired compound. the actual identity of the remaining solution was not confirmed.

At this point a new synthetic procedure was devised (Scheme 2) utilizing 3,4-dihydroxythiophene. 3,4-dihydroxythiophene can be synthesized by adding 2,2'-thiobisacetate ethyl ester to diethyl oxalate in a solution of ethanol and sodium metal, according to the method of Hinsberg, to produce 3,4-dihydroxy-2,5-dicarboxythiophene, compound A in Scheme 3. Hydrolysis of compound A with ethanolic sodium hydroxide results in a dicarboxylic acid, compound B. Heating compound B under a reduced atmosphere causes sublimation of compound C as a yellow

powder. Care must be taken in isolation because compound C decomposes readily on exposure to heat, light and moisture. Alternatively, a more direct approach toward the formation of 3,4-dihydroxythiophene is to add HS^- and a base, or simply S^{2-} , to 1,4-dibromo-2,3-butanedione. Once 3,4-dihydroxythiophene was obtained it was reacted with 2 equivalents of ethyl bromoacetate under basic conditions to form compound D which when treated with 2 equivalents of LDA in the presence of I_2 or another oxidizing agent formed compound F. Alternatively, compound F can be synthesized by adding 3,4-dihydroxythiophene to a cyclic sulfate ethyl ester, compound E, in the presence of potassium tert-butoxide at elevated temperatures. Upon reduction of F with LiAlH_4 compound G was formed. Treatment of G with PBr_3 resulted in the formation of compound H. Conversion of compound H to the desired monomer, I, is accomplished by treatment with potassium thioacetate followed by acidification under aqueous conditions, then I_2 addition to result in the desired monomeric compound I. Alternatively, treatment of compound H with 2 equivalents of ammonium thiocyanate under acidic conditions in the presence of an oxidizing agent, I_2 , also resulted in formation of compound I. The same compound I was also formed by adding 2 equivalents of HS^- and an oxidizing agent to compound H. Polymerization of compound I was accomplished in the presence of FeCl_3 .

Experimental:

2,2'-thiobisacetate ethyl ester. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (14g, 58 mmol) was dissolved in an $\text{EtOH}/\text{H}_2\text{O}$ (60 mL/36 mL) solution. Ethyl bromoacetate was added. This was heated at 80 °C for 19 h under N_2 with an oil bath. Upon cooling to ambient temperature EtOH

was removed *in vacuo* leaving a turbid aqueous solution. Washed with Et₂O (2 x 40 mL), dried the Et₂O layer with MgSO₄. The Et₂O was evaporated under vacuum and the remaining solution was distilled to yield 4.66 g (39%) of a yellow oil. ¹H NMR (C₆D₆, 400 MHz, 23 °C): δ 3.87 (q, 2H; OCH₂CH₃), 3.15 (s, 2H; SCH₂), 0.90 (t, 3H. OCH₂CH₃).

2,5-dicarbethoxy-3,4-dihydroxythiophene. Diethyl oxalate (6.58 g, 45 mmol) was added to 2,2' thiobisacetate ethyl ester (4.66 g, 23 mmol) to produce a yellow-orange solution. A solution of Na (1.56 g, 68 mmol) in EtOH (24 mL) was added to produce a white/yellow precipitate, this was mixed well for 10 minutes. H₂O (50 mL) was added to the reaction mass with cooling in an ice bath. Concentrated HCl was added dropwise until acidified. This was allowed to stand in the refrigerator for 12 days. At this point a cold filtration was done to isolate a white solid.

2,5-dicarboxy-3,4-dihydroxythiophene. EtOH (30 mL) was added to 2,5-dicarbethoxy-3,4-dihydroxythiophene (1 g). A solution of NaOH (4.0 g) in H₂O (20 mL) was added and refluxed under N₂ for 20 h. Upon cooling to ambient temperature the EtOH was removed by distillation and the residue was redissolved in H₂O then acidified with 15 % HClaq when a white ppt was obtained. This product was collected by filtration and washed with cold H₂O then crystallized from dilute MeOH to give colorless needles.

3,4-dihydroxythiophene. The acid, 2,5-dicarboxy-3,4-dihydroxythiophene (1g), was sublimed in a sublimation tube at 120 °C/3mm. The yellowish decarboxylated product was resublimed and then crystallized from benzene and ligroin to give pale yellow needles.

Cyclic sulfate ethyl ester. Carbon tetrachloride (25 mL) was added to diethyl-L-tartrate (4.3 mL, 25 mmol). Thionyl chloride (3.57 g, 30 mmol) was added via syringe slowly and the solution was refluxed for 50 min. then cooled in an ice bath and diluted with CH₃CN (25 mL). RuCl₃·3H₂O (8 mg, 0.03 mmol) and H₂O (38 mL) were added, followed by NaIO₄ (16 g, 75 mmol). The mixture was stirred at room temperature for 17 h. The mixture was then diluted with 200 mL Et₂O and the two phases were separated. The organic layer was washed with H₂O (10 mL), saturated NaHCO₃ (2 x 20 mL), and brine (10 mL). After drying over MgSO₄, the solution was filtered through a small pad of silica gel. The filtrate was then concentrated to yield analytically pure colorless crystals.

Example 2

The use of 3,4-dihydroxythiophene is also necessary in the synthesis of the second desired monomeric component shown in figure 2 and will be synthesized as described above. Scheme 4 shows the mechanism of formation of the compound shown in figure 2. The reaction of 3,4-dihydroxythiophene with 2,2-dimethyl-1,3-dioxolane-4-methanol in the presence of a base, followed by H₃O⁺ addition, resulted in the formation of compound K. Alternatively, this is also formed by the addition of 2 equivalents of allyl bromide to 3,4-dihydroxythiophene in the presence of a base. The resulting product, J, was treated with catalytic amounts of OsO₄ and sodium periodate to produce compound K. Once compound K was obtained it was treated with PBr₃ or tosyl chloride to form L, where LG = Br or OTs. Compound L can also be produced by the addition of 1,2,3-tribromopropane to 3,4-dihydroxythiophene. Treatment of L with potassium thioacetate

resulted in formation of M. Polymerization of this material was done in the cathode assembly step followed by removal the thioacetate protecting groups during curing of the cathode, through the use of lithium hydroxide. Alternatively, compound N can be reached directly by treating compound L with HS^- and an oxidizing agent. At this point polymerization of N was accomplished electrochemically.

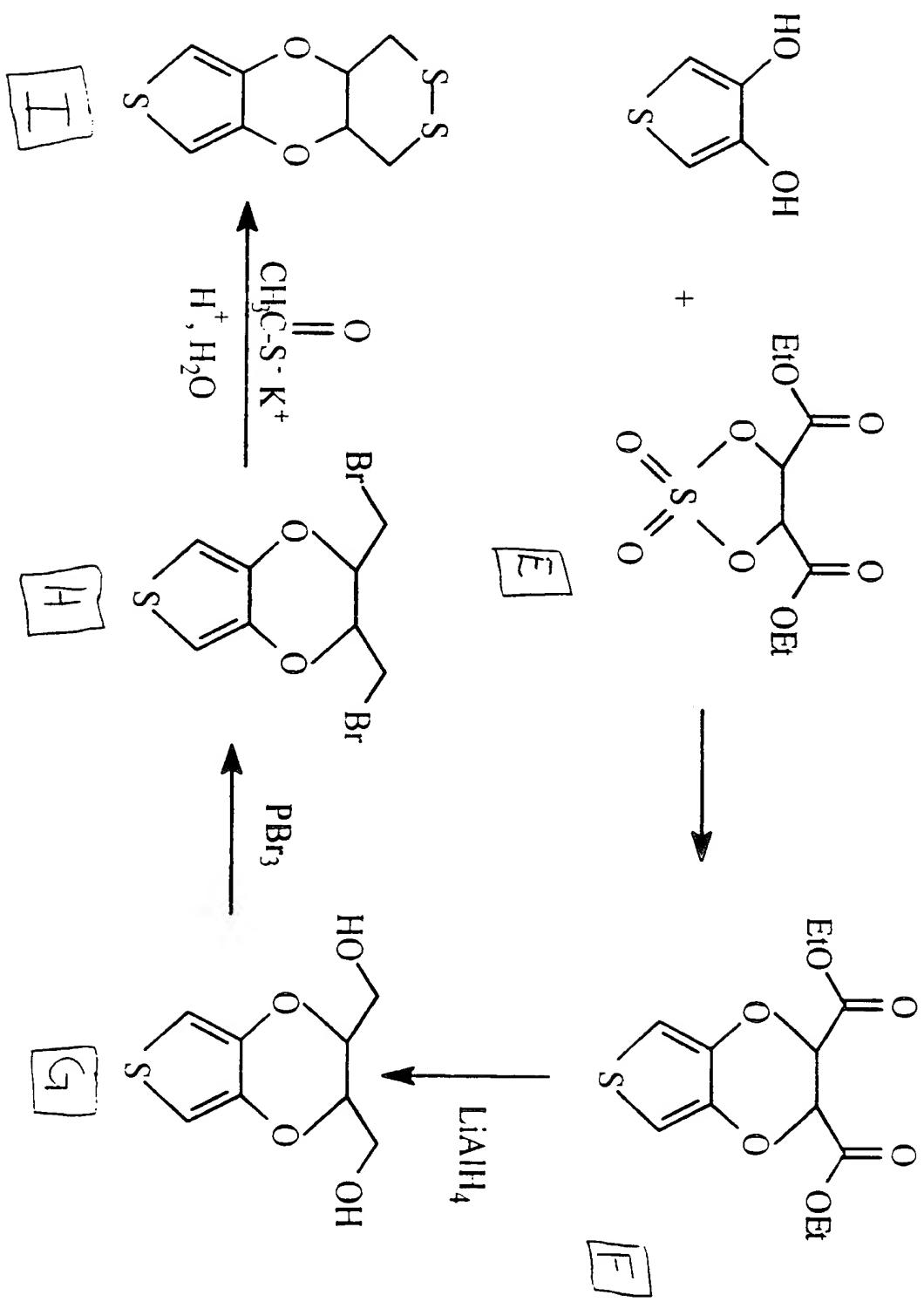
Experimental:

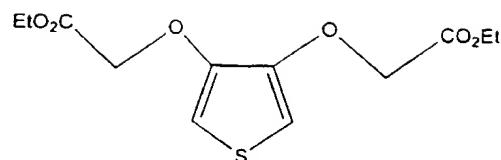
2,2'-thiobisacetate ethyl ester. $Na_2S \cdot 9H_2O$ (14g, 58 mmol) was dissolved in an $EtOH/H_2O$ (60 mL/36 mL) solution. Ethyl bromoacetate was added. This was heated at 80 °C for 19 h under N_2 with an oil bath. Upon cooling to ambient temperature $EtOH$ was removed *in vacuo* leaving a turbid aqueous solution. Washed with Et_2O (2 x 40 mL), dried the Et_2O layer with $MgSO_4$. The Et_2O was evaporated under vacuum and the remaining solution was distilled to yield 4.66 g (39%) of a yellow oil. 1H NMR (C_6d_6 , 400 MHz, 23 °C): δ 3.87 (q, 2H; OCH_2CH_3), 3.15 (s, 2H; SCH_2), 0.90 (t, 3H, OCH_2CH_3).

2,5-dicarbethoxy-3,4-dihydroxythiophene. Diethyl oxalate (6.58 g, 45 mmol) was added to 2,2' thiobisacetate ethyl ester (4.66 g, 23 mmol) to produce a yellow-orange solution. A solution of Na (1.56 g, 68 mmol) in $EtOH$ (24 mL) was added to produce a white/yellow precipitate, this was mixed well for 10 minutes. H_2O (50 mL) was added to the reaction mass with cooling in an ice bath. Concentrated HCl was added dropwise until acidified. This was allowed to stand in the refrigerator for 12 days. At this point a cold filtration was done to isolate a white solid.

2,5-dicarboxy-3,4-dihydroxythiophene. $EtOH$ (30 mL) was added to 2,5-dicarbethoxy-3,4-dihydroxythiophene (1 g). A solution of NaOH (4.0 g) in H_2O (20 mL) was added

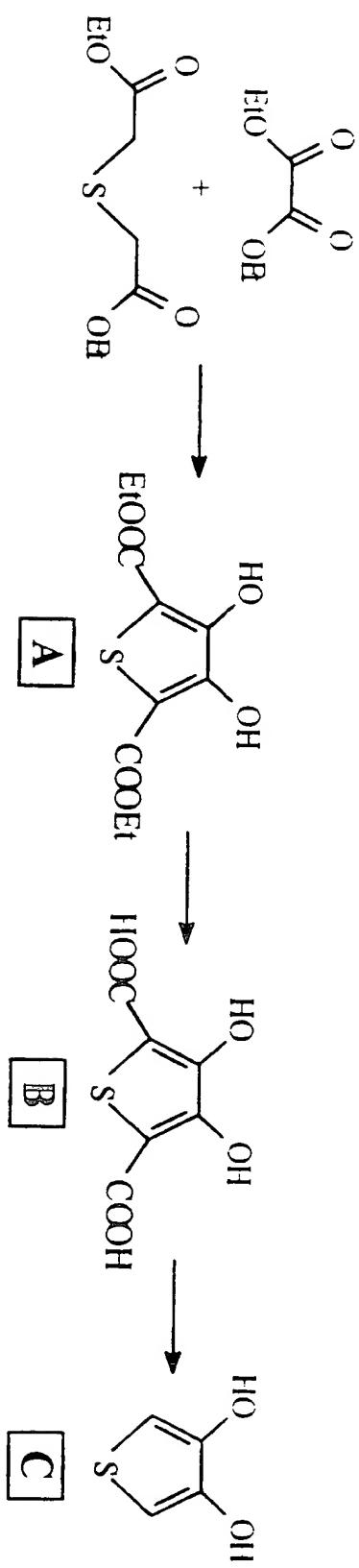
Scheme 2



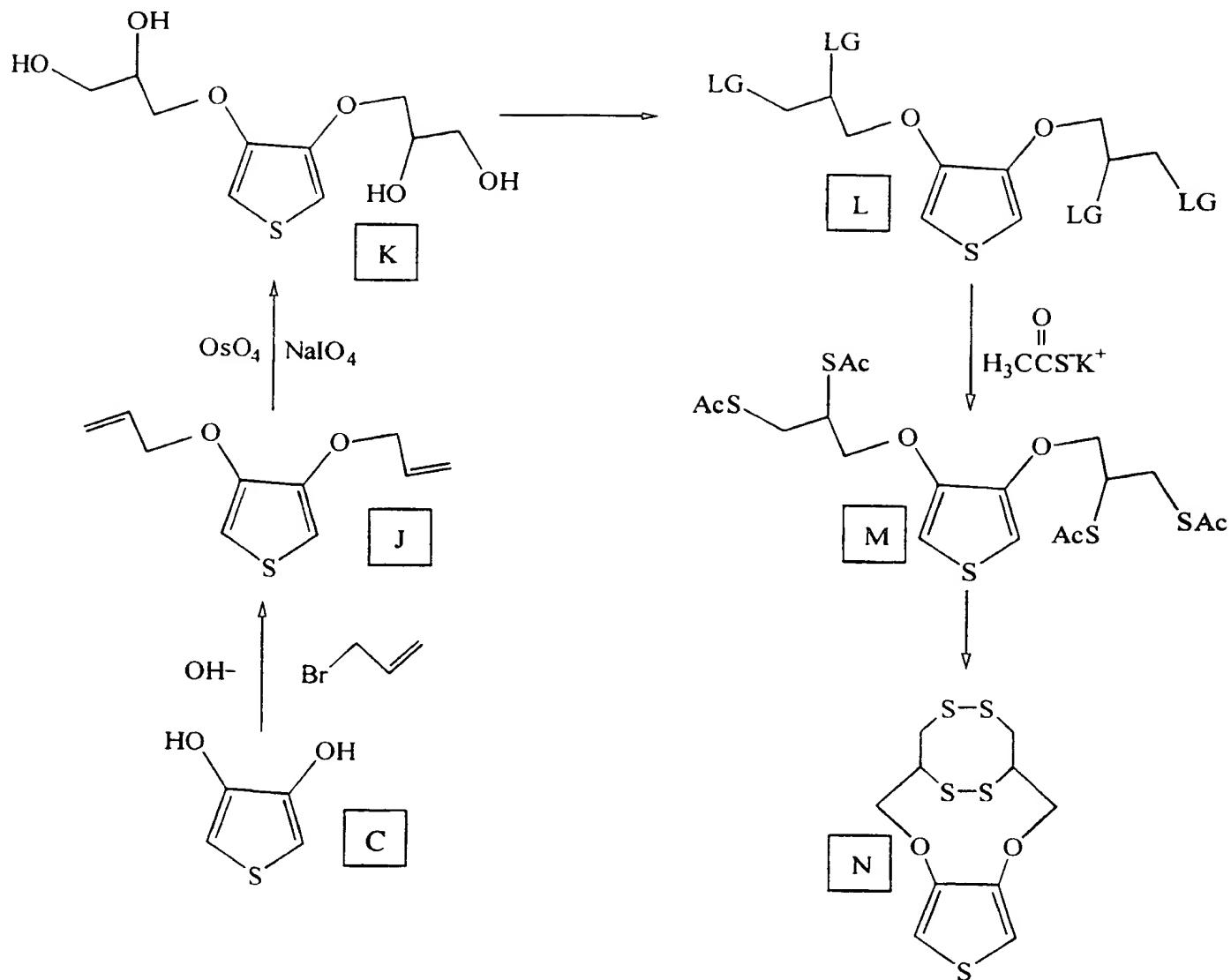


D

Scheme 3.



Scheme 4



and refluxed under N₂ for 20 h. Upon cooling to ambient temperature the EtOH was removed by distillation and the residue was redissolved in H₂O then acidified with 15 % HClaq when a white precipitate was obtained. This product was collected by filtration and washed with cold H₂O then crystallized from dilute MeOH to give colorless needles.

3,4-dihydroxythiophene. The acid, 2,5-dicarboxy-3,4-dihydroxythiophene (1g), was sublimed in a sublimation tube at 120 °C/3mm. The yellowish decarboxylated product was resublimed and then crystallized from benzene and ligroin to give pale yellow needles.

CLAIMS

- 1) A method of selecting cathode materials for a sulfur-based Lithium battery wherein the cathode comprises a conducting polymer and a sulfur species:
 - identifying a characteristic of the conducting polymer;
 - identifying a characteristic of the sulfur species;
 - evaluating the characteristic of the conducting polymer and the sulfur species;
 - selecting the conducting polymer and the sulfur species based on the identified characteristic;

wherein the identified characteristic of the sulfur species and the identified characteristic of the conducting polymer are at least one characteristic selected from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; a high density of electroactive species per weight and volume/large inherent charge capacity $> 230 \text{ Ah/kg}$; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer; reasonable electronic conductivity (10^4 S/cm) of the cathode materials; no solubility in electrolyte solutions; or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.
- 2) The method of claim 1 wherein the identified characteristics are all of the at least one characteristics.

3) The method of claim 1 wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer.

4) The method of claim 1 wherein the at least one characteristic is no solubility in electrolyte solutions.

5) A cathode material for use in a sulfur-based Lithium battery comprising a sulfur species and a conducting polymer;

wherein the conducting polymer and the sulfur species exhibit at least one characteristic selected from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; a high density of electroactive species per weight and volume/large inherent charge capacity $> 230 \text{ Ah/kg}$; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer; reasonable electronic conductivity (10^4 S/cm) of the cathode materials; no solubility in electrolyte solutions; or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.

6) The cathode material of claim 5, wherein the at least one characteristic includes all of the characteristics from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; a high density of electroactive species per weight and volume/large inherent charge capacity $> 230 \text{ Ah/kg}$; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer;



reasonable electronic conductivity (10^{-4} S/cm) of the cathode materials: no solubility in electrolyte solutions: or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.

7) The cathode material of claim 5, wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer.

8) The cathode material of claim 5, wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer and no solubility in electrolyte solutions.

9) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species and a conducting polymer wherein the conducting polymer is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer.

10) The cathode material of claim 9, wherein the covalent link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte.

11) The cathode material of claim 9, wherein the electrolyte contains no other sulfur or other sulfur species except for the linked sulfur species.

12) The cathode material of claim 9, wherein the cathode material is a thiophene based polymer with the covalently linked sulfur species.

13) The cathode material of claim 9, wherein the conducting polymer are covalently-derivatized with sulfides and/or sulfide-containing groups.

14) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species including sulfide components and a conducting polymer wherein the conducting polymer is a single component sulfur-based conducting polymer wherein physical constraints of the conducting polymer and the sulfide components via covalent bonds which are present regardless of charge state of the cathode material.

15) An electric current producing cell comprising:

- a) an anode;
- b) a cathode containing a cathode material of claim 14; and,
- c) an electrolyte between the anode and cathode.

16) An electric current producing cell comprising:

- a) an anode;
- b) a cathode containing a cathode material of claim 12; and,
- c) an electrolyte between the anode and cathode.

17) An electric current producing cell comprising:

- a) an anode;
- b) a cathode containing a cathode material selected by the method of claim 2; and,
- c) an electrolyte between the anode and cathode.

18) The cathode material of claim 13, wherein the sulfur-derivatized conducting polymer is represented by a formula $(R_i)_n(Y_jA_k)_m$ (where R is monomer or oligomer units of the conducting polymer, i is 1 to n and n is greater than 20, Y is a functionalizing group that provides additional physical or chemical properties to the conducting polymer and j is 0 to n; A is the sulfur species, k is 1 to n and m is 1 to 12.

19) The cathode material of claim 18, wherein n is greater than 1000.

20) The cathode material of claim 19, wherein n is greater than 100,000.

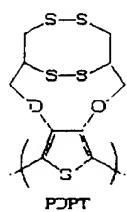
21) The cathode material of claim 13, wherein the sulfur-derivatized conducting polymer is represented by a formula $(R)_n(YS_m)_x$ (where R is a conducting polymer backbone and n is greater than 20; Y is a functionalizing group; S is an organosulfur moiety, m is 1 to 12 and x is 1 to 4.

22) The cathode material of claim 21, wherein n is greater than 1000.

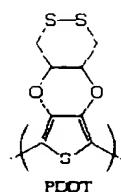
23) The cathode material of claim 22, wherein n is greater than 100,000.

24) The cathode material of claim 21, wherein R is polythiophene or its derivatives.

25) The cathode material of claim 24, wherein the single component sulfur-based conducting polymer is represented by:



26) The cathode material of claim 24, wherein the single component sulfur-based conducting polymer is represented by:



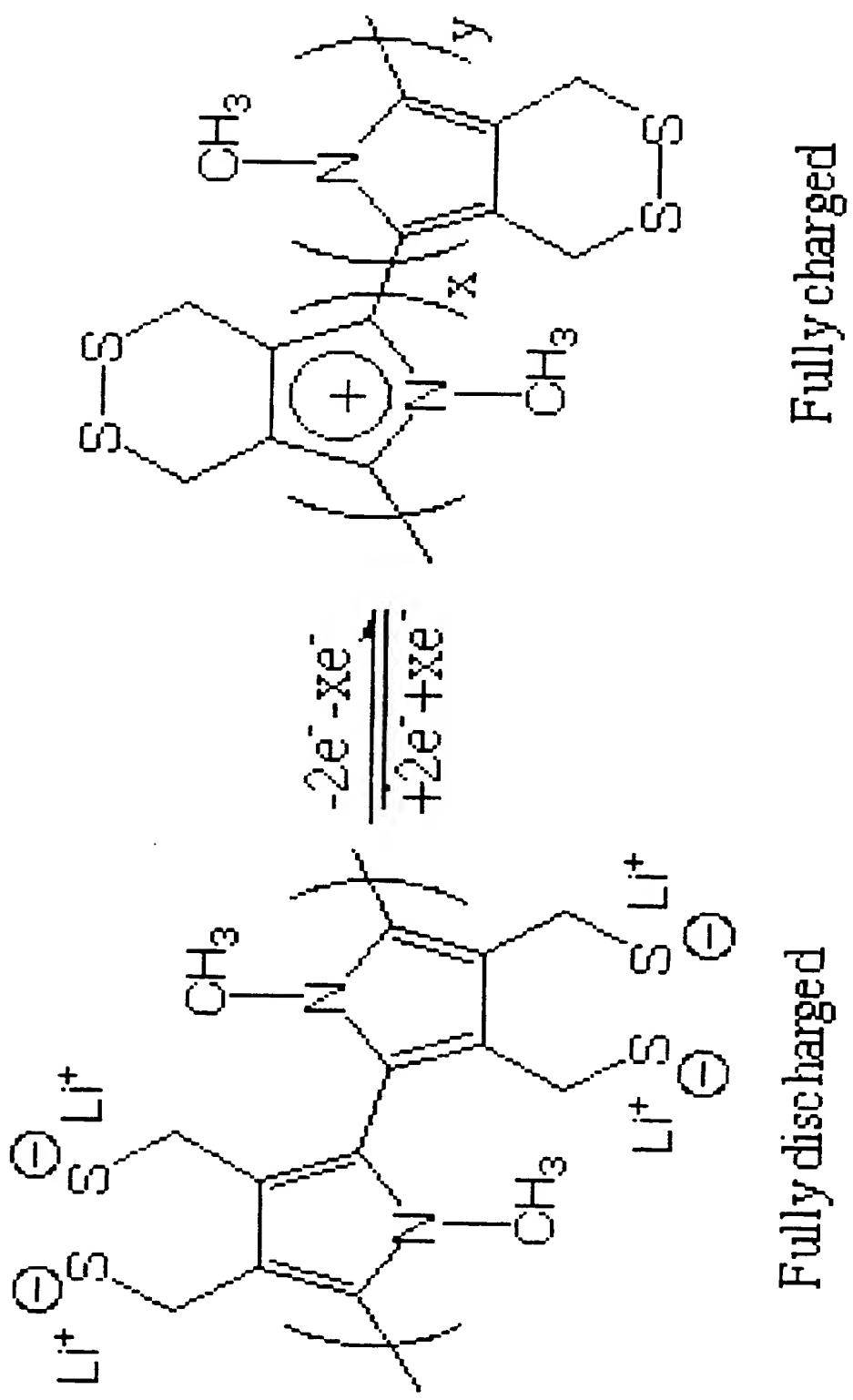


Figure 1

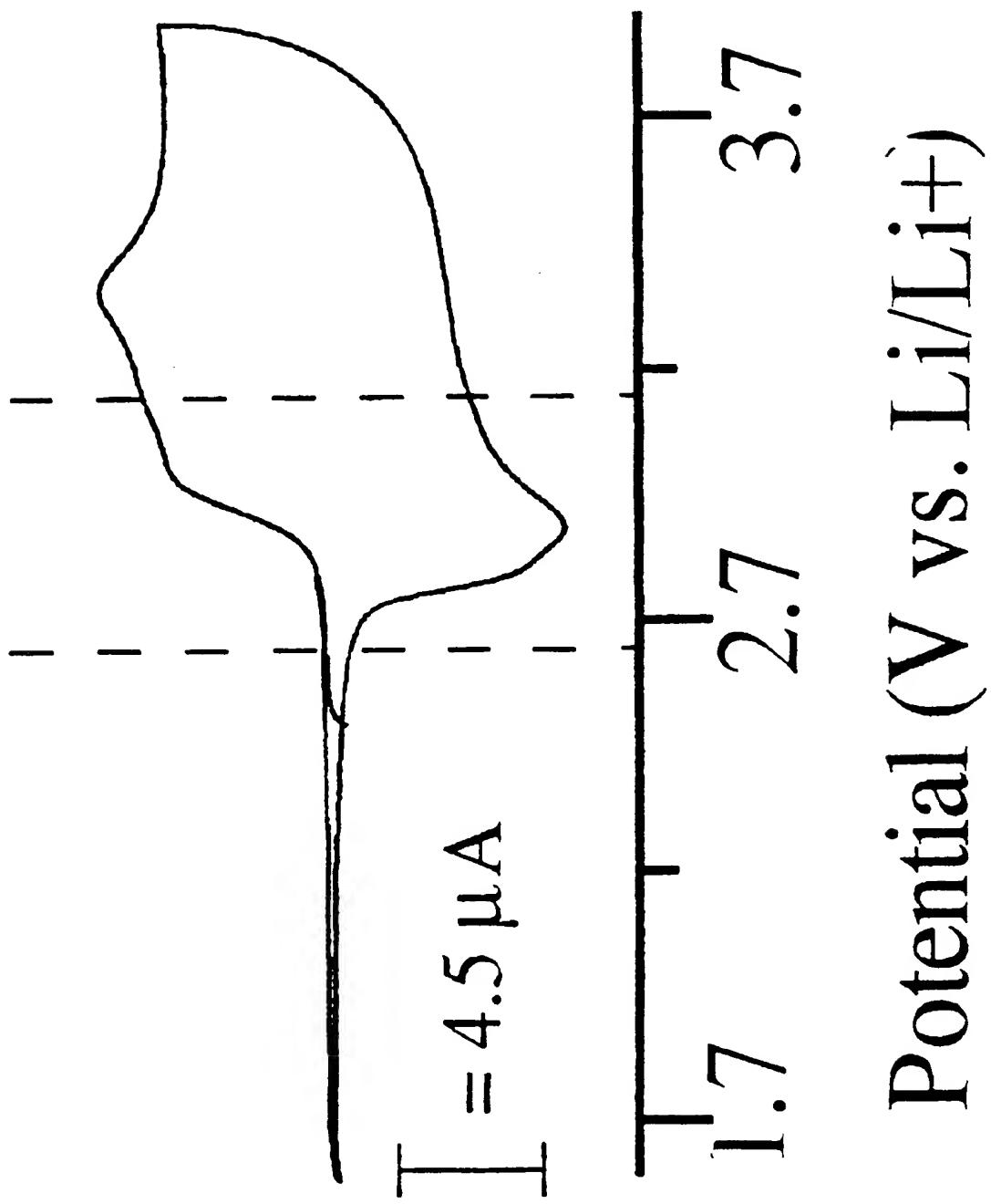


Figure 2

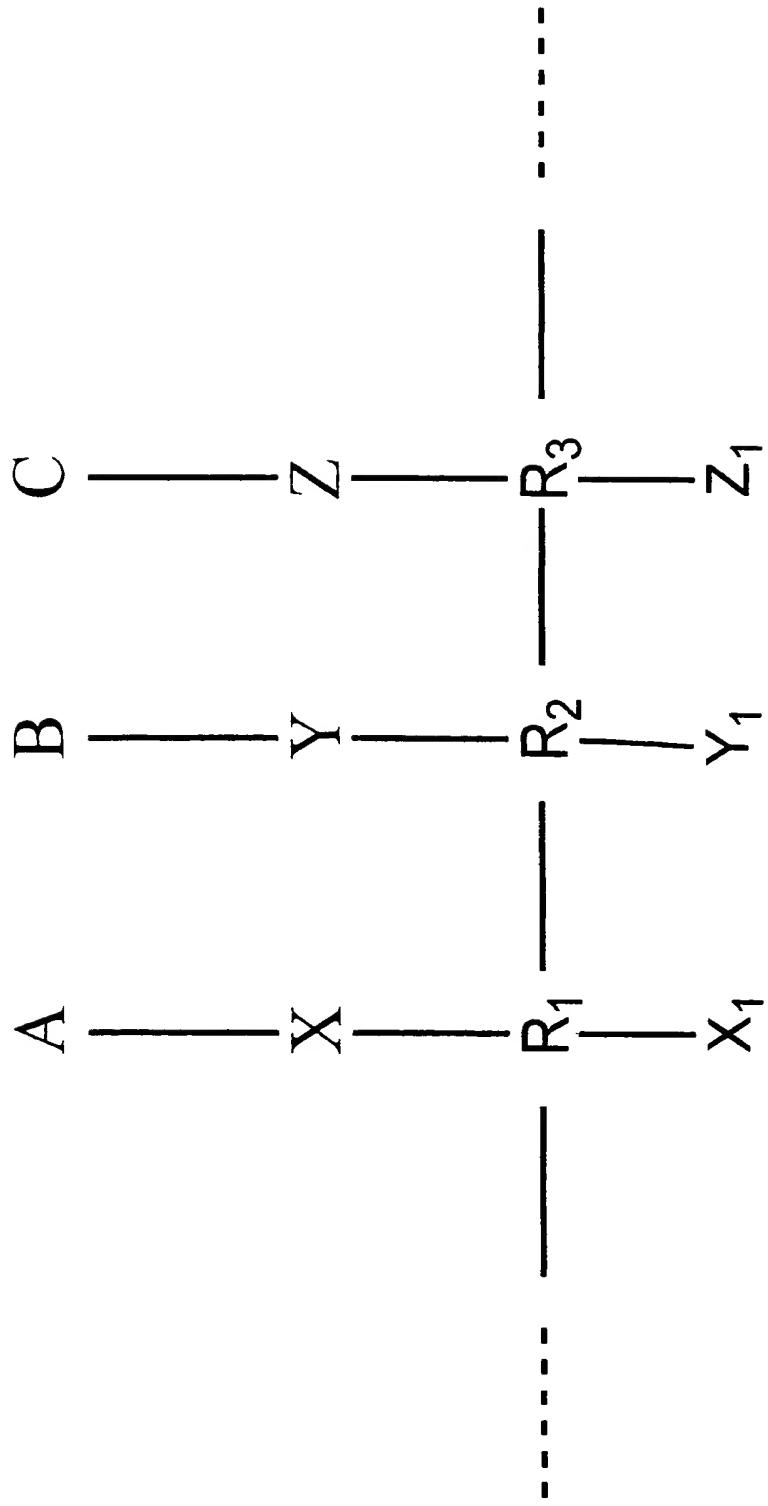


Figure 3

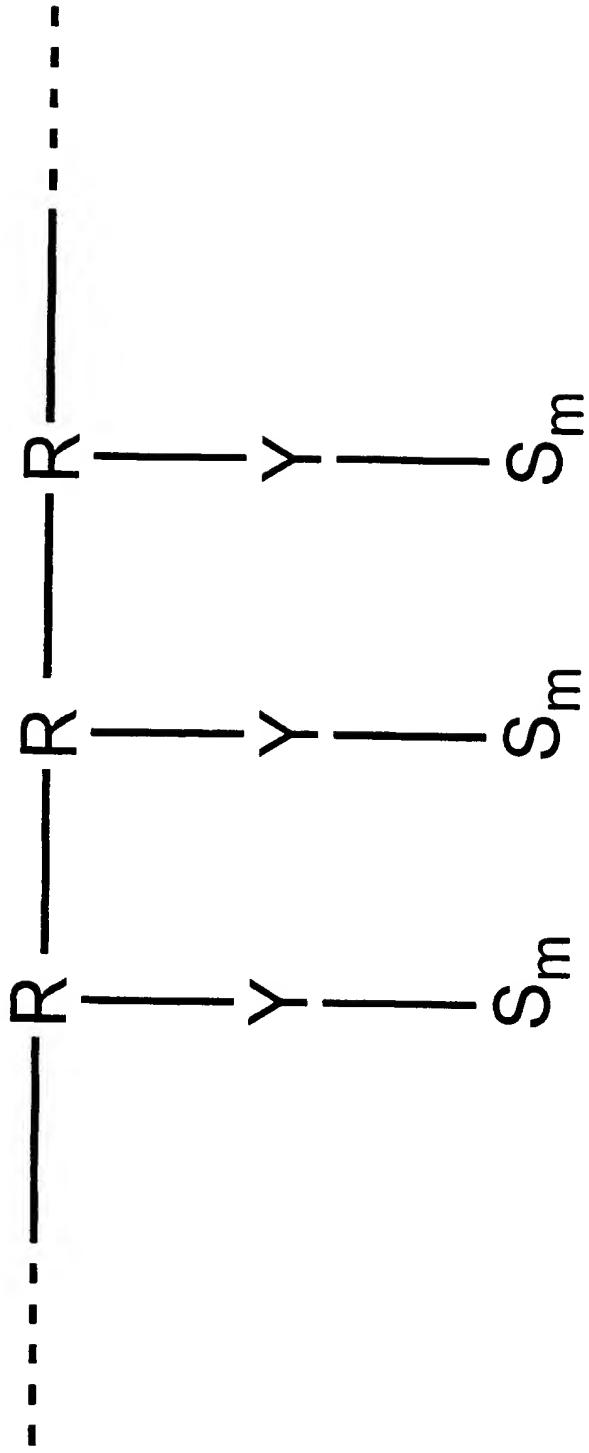


Figure 4

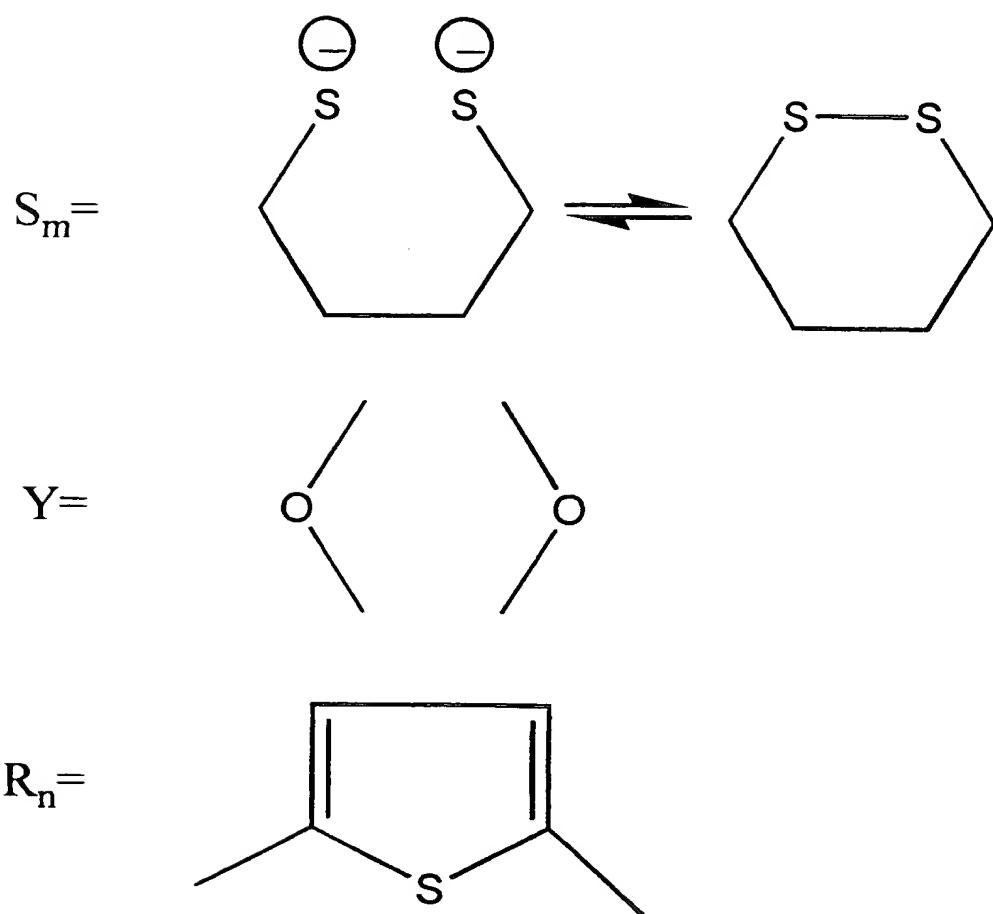
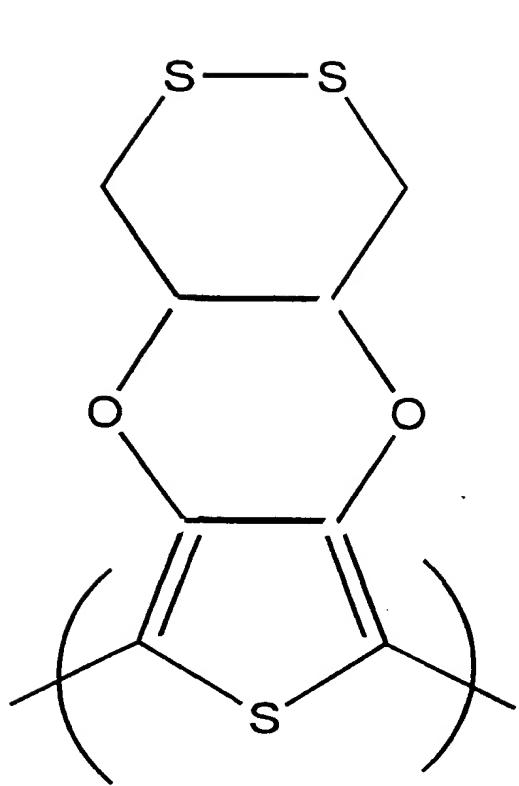
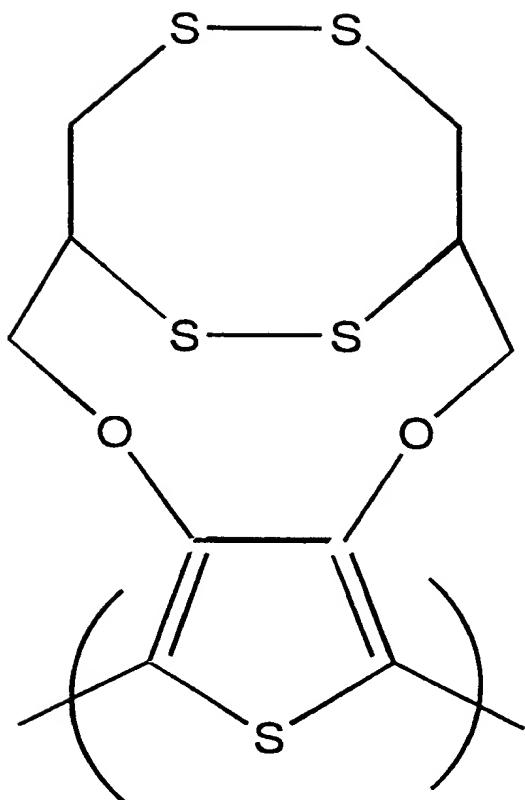


Figure 5



PDDT



PDPT

Figure 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/02445

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01M 4/60
US CL :429/213

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/213

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST, Non-Patent Literature (Elsevier Science Search)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,472,488 A (MAXFIELD et al.) 18 September 1984, col. 4, lines 47-54.	9-24
X	US 5,723,230 A (NAOI et al.) 03 March 1998, col. 10, lines 16-36.	9-23
X	US 5,712,057 A (FAUTEUX) 27 January 1998, col. 2, lines 47-56.	9-23
A	US 4,869,979 A (OHTANI et al.) 26 September 1989, the entire document.	9-26

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

02 JUNE 2000

Date of mailing of the international search report

15 JUN 2000

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(72) Inventors; and

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(54) Title: SINGLE COMPONENT SULFUR-BASED CATHODES FOR LITHIUM AND LITHIUM-ION BATTERIES

(57) Abstract: The present invention pertains to the selection of cathode materials. The cathode materials of concern are the conducting polymer or backbone and the redox active species or sulfur species. The selection of the materials is based on the characteristics of the materials relating to the other components of the batteries and to each other. The present invention also pertains to the resultant cathode materials, particularly a selected cathode material of a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer, and most particularly a thiophene based polymer with covalently linked sulfur species. The conducting polymers have been covalently-derivatized with sulfides and/or sulfide-containing groups as battery cathode materials. The present invention also pertains to a battery employing the selection method and resultant cathode materials.

SINGLE COMPONENT SULFUR-BASED CATHODES FOR
LITHIUM AND LITHIUM-ION BATTERIES

RELATED APPLICATIONS

This application claims priority to U.S. Provisional patent application 60/118,068, the contents of which are incorporated herein by reference in their entirety.

TECHNICAL FIELD

The present invention relates generally to cathodes for rechargeable batteries. More particularly, the present invention relates to cathode materials based on conducting polymers and sulfur or selenide species and the method of selecting conducting polymers and sulfur or selenide species. The selection method accounts for characteristics of the conducting polymer and the sulfur or selenide species and the specific capacity, capacity fade, charge and discharge rate, physical and chemical stability, safety and other characteristics associated with battery cycles. More particularly, the present invention relates to a single component sulfur-based conducting polymer for use in lithium batteries and the synthesis of such material.

BACKGROUND

Increasing reliance on sophisticated electronic technologies has exacerbated a need for reliable, portable sources of energy. The current worldwide market for rechargeable batteries exceeds \$4 billion. However, an estimated \$6 billion market in the United States alone remains untapped due to the inability of available products to meet the needs of a large industrial, consumer, and military based market. And the need is growing, particularly for high power applications such as electric vehicles and load-leveling equipment and weight or volume constrained applications such as portable computers, cellular phones, etc. Creative alternatives to current battery technologies must be developed.

Among available technologies, lithium and lithium-ion batteries represent the most promising technologies, especially in terms of their attractive energy densities when compared to nickel cadmium and nickel-metal hydride cells. This promise can be attributed in large part to the extremely high specific capacity available in theory from lithium (3862 A h/kg) and the reasonable charge capacity available from lithium-intercalated carbon (e.g. for LiC_6 , 372 A h/kg) anodes.

However, realization of the full potential of that technology has been awaiting development of 1) electrolyte compositions able to withstand the high reactivities of those

anodes, and 2) inexpensive, stable cathodic materials also able to store high charge capacities. The present invention addresses resolution of the latter issue.

Batteries currently marketed utilize LiCoO₂ cathodes, a material that has a theoretical specific capacity of 274 A h/kg and a practical specific capacity of 100 to 150 A h/kg. In realistic terms, then, cells using LiCoO₂ can utilize only one-thirtieth of the potential energy per gram stored in lithium metal (or only one-third of the potential energy per gram stored in LiC₆). While batteries based on such cathodes are suitable to meet short-term commercial needs, significant progress in this area must be based around developing cathodes with specific capacities similar to those of the best available anodes.

In terms of alternative cathode materials being currently studied, sulfur and sulfur-containing compounds offer the best opportunities in terms of high theoretical specific capacities. Sulfur cathodes operate by storing energy as disulfide bridges, a very stable oxidized material, then releasing it by reducing to thiolate moieties. This process is illustrated in Figure 1 for one material. While sulfur cathodes were the first employed for lithium laboratory cells, their use in practical batteries was abandoned primarily due to the insulating nature of those materials, which necessitates using high temperatures in order to facilitate mass transport within the cathodes.

However, advances in understanding and controlling electronic conductivity in composite materials has signaled a revival of that class of materials, as evidenced by ongoing exploratory or commercial efforts. Experimental lithium metal and lithium ion anode

prototypes of systems recently developed match or exceed current room temperature secondary battery performances in terms of gravimetric energy density (energy delivered per mass of the cathode material).

In U.S. Patent No. 5,789,108, Chu is pursuing technology based on cathodes composed of inorganic sulfur mixed with poly(ethylene oxide) (PEO), lithium salts, and carbon powders, while Skotheim et al., in U.S. Patent No. 5,529,860, are developing cathodes based on inorganic sulfur and poly(acetylene) derivatives. Those formulations represent attempts at achieving electronic and ionic access to the sulfur in those cathode *via* dispersion in an ionically conducting medium (PEO) which contains an electronic conductor (carbon)(Chu) or the use of a conducting polymer to effect both goals (Skotheim et al.).

Although such materials show excellent specific capacities during initial cycles, neither Chu nor Skotheim et al. have commercialized a sulfur or organosulfur based secondary battery due to high capacity loss, or "fade," observed for their cells over multiple charge and discharge cycles. Consideration of the possible origins of that behavior are obscured by a general lack of knowledge regarding the complicated electrochemistry of inorganic sulfur, compounded by the varying solubilities and chemical activities of the different forms of sulfur (e.g. polysulfide, oligosulfide, dimer, monomer (S^{2-})), possible reaction between those species and the anode, and the likely growth of heterogeneous zones of non-conductive material that separate from the initial cathode mixture.

However, it is clear from recent work that the capacity fade observed is due in large part to diffusion of monomeric sulfur species out of the cathode. While interesting redox chemistry is typically evident in the first few cycles, it typically fades after several cycles to leave less desirable redox activity – *viz.* the organosulfur or sulfur or selenide component exits the cathode *via* dissolution into the electrolyte film, resulting in capacity loss during cycling.

In WO 99/03162, Skotheim et al., describe a polymer film that protects the lithium anode in a secondary battery. The film interferes to some degree with the reactions and thus reduces the overall efficiency of the battery. The film is needed when sulfur species are mobile and may migrate to the anode. Skotheim et al. do not suggest decreasing or eliminating the mobility of reactive sulfur species so that interference at the anode is decreased and thereby the efficiency of the battery is increased.

Definitions

Conducting polymer:

Conducting polymers are polymers through which electrons can move from one end of the polymer to the other. A conducting polymer transports voltage and/or current along its backbone or between its chains by changing the distribution of electrons in the polymer

chain. Such conduction typically occurs through conjugated π electronic functionalities, although some conducting polymers include other types of electronic functionalities. In some instances, conductivity occurs in short chains of the polymer (“oligomers”). In some cases, conductivity occurs in long chains of the polymer. Non-limiting examples of conducting polymers include poly(acetylene), poly(aniline), poly(pyrrole), poly(thiophene), poly(*p*-phenylene), (poly)phthalocyanine, etc. and derivatives thereof.

Redox species:

A redox species is an atom, molecule, or macromolecule that accepts or releases one or more electrons when placed under an electric field of appropriate direction and magnitude. Non-limiting examples of redox species include ruthenium hexamine chloride, ferrocene, gold, poly(pyrrole), hexanethiol, and similar species and derivatives.

Battery:

A battery is comprised of one or more cells each comprised of an electropositive anode such as lithium or nickel, an electronegative cathode such as metal oxide, sulfur, or cadmium, and an ionically-conducting separator, such as poly(ethylene oxide), propylene carbonate, or Nafion, that contain an electrolytic salt such as lithium hexafluorophosphate, sodium chloride, etc. A cell “discharges” by allowing electrons to pass via an external circuit

from a higher energy state in the anode to a lower energy state in the cathode while allowing ions to pass through the separator. In lithium-based cells, Li ions pass from the anode through the separator to the cathode. The electrons that pass through the external circuit may be used to perform work. In a rechargeable battery, this electron and ion movement may be reversed to some extent by applying an external current to the cell to "charge" the cell. The typical forms of batteries, and more specifically of lithium-based batteries are well known to those skilled in the art.

Sulfur species:

In this document, sulfur species include atoms, molecules, and macromolecules that contain at least one sulfur atom. Typical terms used to describe such molecules include organosulfur, sulfur, sulfide, disulfide, thio, thiol, thiolate, mercapto, mercaptan, etc. In some cases, the sulfur species contains a negatively-charged or proton-associated sulfur atom that is covalently bound to another atom through a single bond. This type of sulfur species is capable of releasing an associated cation or proton and forming a disulfide bond with a similar atom. In other cases, the sulfur species contains sulfur atoms that are multiply bound to other atom or atoms and are not capable of forming disulfide bonds. In all cases, in this document, sulfur species refers to atoms, molecules, and macromolecules that contain at least one sulfur atom that can act in part or in whole as a redox species.

Selenium species

In this document, selenium species include atoms, molecules, and macromolecules that contain at least one selenium atom. Typical terms used to describe such molecules include selenide, selenate, diselenides, etc. In some cases, the selenide species contains a negatively-charged or proton-associated selenide atom that is covalently bound to another atom through a single bond. This type of selenide species is capable of releasing an associated cation or proton and forming a diselenide bond with a similar atom. In other cases, the selenide species contains selenide atoms that are multiply bound to other atom or atoms and are not capable of forming diselenide bonds. In all cases, in this document, selenide species refers to atoms, molecules, and macromolecules that contain at least one selenide atom that can act in part or in whole as a redox species.

SUMMARY OF INVENTION

One aspect of the present invention pertains to the selection of cathode materials. The cathode materials of concern are the conducting polymer or backbone and the redox active species or sulfur species. The selection of the materials is based on the characteristics of the materials relating to the other components of the batteries and to each other.

In one embodiment, the selection of cathode materials is based on one or more of the following characteristics of the conducting polymer and/or the sulfur or selenide species: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li⁺ ions; no labile protons in the material; a high density of electroactive species per weight and volume (i.e. large inherent charge capacity); good overlap of the thermodynamic redox potentials of the electroactive substituents and the conducting polymer backbone; reasonable electronic conductivity of the composite; no solubility in typical electrolyte solutions; and electrochemically, physically, and chemically stable to many repeated charge and discharge cycles. In a preferred embodiment, the selection of the cathode materials is based on all of the above identified characteristics for both the conducting polymer and the sulfur or selenide species.

In one embodiment, the selection of cathode materials is based on the overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials are chosen based on the redox mediation window. The conducting polymer mediates electrons between the current collector and the sulfur or selenium species. Conducting polymers exhibit potential-dependent conductivities. When the potential is in the "double-layer" region of the conducting polymer (that is, when the conducting polymer is releasing or accepting electrons), the conductivity of the polymer is much higher than when the potential is more negative or more positive of that region. If the conducting polymer is inherently in a less-conductive state in the potential region where the sulfur or selenium species exhibits redox species behavior, mediation of electrons between

the current collector and the sulfur or selenium species is poorly effected, the material is less desirable, and the battery performance is poorer.

In a preferred embodiment, the resulting premise of the selection process of materials is that the redox active species or sulfur species that are mobile are not compatible with long-life, high-capacity batteries.

Another aspect of the present invention pertains to resultant cathode materials identified by the use of the selection process identified above.

In a preferred embodiment, the cathode materials were selected because they exhibit overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials form a redox mediation window. The conducting polymer mediates electrons between electrode(s) and the sulfur species in an effective fashion.

In a preferred embodiment, the sulfur species is NOT covalently linked to the conducting polymer backbone. An example of this system is that comprising a mixture of poly(3,4-ethylenedioxythiophene) (PEDT) and 2,5-dimercapto-1,3,4-thiadiazole, dilithium salt (Li₂DMcT). PEDT is available as an aqueous dispersion. Li₂DMcT is dissolved directly into the PEDT dispersion at high concentrations. Properly treated films cast from that mixture are used as cathode materials in lithium and lithium-ion cells. Alternately, films are

prepared by electrochemical or chemical oxidation of the PEDT monomer and Li₂DMcT from the same or different solutions in a homogeneous or layered arrangement. Li₂DMcT contains no labile protons, so its use in the cathode is attractive. PEDT has a wide potential window of conductivity, contains no labile protons, and is not proton-doped, so its use in the cathode is attractive.

One embodiment of the present invention is the cathode materials are not mobile. Specifically, the redox active species or sulfur species is not mobile. The redox active species is bound to the conducting polymer and is not able to migrate from the conducting polymer.

In a preferred embodiment, the cathode material is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer. The link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte. In this preferred embodiment, sulfur or other sulfur species apart from the covalently linked sulfur species may or may not be present. Most preferably the cathode material contains no other sulfur or sulfur species apart from the bound sulfur species.

In a preferred embodiment, the cathode material is a thiophene based polymer with covalently linked sulfur species. Such conducting polymers have been covalently-derivatized with sulfides and/or sulfide-containing groups and employed as battery cathode materials. Physical constraints of the conducting polymer and sulfide components via covalent bonds which are present regardless of charge state of the cathode represents a novel step in the field.

Yet another aspect of the present invention pertains to a method of synthesis of the selected cathode material.

Still another aspect of the present invention pertains to batteries which comprise an anode; cathode material(s) of the present invention, as described herein; and a separator between the anode and the cathode materials

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 shows a sulfur cathode in operation by storing energy as a disulfide bridge then releasing it by reducing to thiolate moieties.

Fig. 2 shows an example of an inappropriate overlap of thermodynamic potentials between polyaniline and an organosulfur.

Fig. 3 shows a general formula of a conducting polymer of the present invention.

Fig. 4 shows a more specific formula of the present invention.

Fig. 5 shows the substituent parts of the polythiophene conducting polymer.

Fig. 6 shows two resultant conducting polymers of the present invention.

DETAILED DESCRIPTION OF INVENTION

One aspect of the present invention pertains to the selection of cathode materials. The cathode materials of concern are the conducting polymer or backbone and the redox active species or sulfur species. The selection of the materials is based on the characteristics of the materials relating to the other components of the batteries and to each other.

In one embodiment, the selection of cathode materials is based on one or more of the following characteristics of the conducting polymer and/or the sulfur species: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; no labile protons in the material; a high density of electroactive species per weight and volume; good overlap of the thermodynamic potentials of the electroactive substituents and conducting polymer backbone; reasonable electronic conductivity of the composite; no solubility in typical electrolyte solutions; and electrochemically stable to many repeated charge and discharge cycles. In a preferred embodiment, the selection of the cathode materials is based on all of the above identified characteristics for both the conducting polymer and the sulfur species.

Molecular design of innovative sulfur-based cathode materials

The chemical and physical constraints imposed on cathode materials are substantial. The specific properties required include ease of fabrication using straightforward synthetic procedures.

In sulfur-based batteries, the sulfur species and preferably the conducting polymer must be ionically conductive for Li^+ ions. The chemistry of sulfur-based batteries necessitates the requirement of the cathode materials to be ionically conductive for Li^+ ions.

A material that contains mobile redox species presents stability, capacity fade, and safety problems when used as a cathode material in a lithium or lithium-ion or lithium polymer cell. For example, 2,5-dimercapto-1,3,4-thiadiazole contains two labile protons. Use of that material as a component of a cathode material leads to transport of the labile protons via intermediate species into the electrolyte and eventually to the anode, where spontaneous electrochemical reduction by the anode creates hydrogen gas. Similar events can occur when poly(aniline), a proton-doped conducting polymer, is used as a component of a cathode material. This constraint includes the selection of conducting polymers and sulfur species that do not contain labile protons at any stage of the battery reaction.

A battery's effectiveness is attributable to the charge capacity. Selecting a sulfur species and conducting polymer with a high density of electroactive species per weight and

volume (i.e. large inherent charge capacity) increases the effectiveness of the cathode and battery overall.

A battery's effectiveness is also dependent on the electronic conductivity of the cathode materials. Selecting a sulfur species and conducting polymer with an electronic conductivity above 10^{-6} S/cm, more preferably above 10^{-5} S/cm, more preferably above 10^{-4} S/cm, more preferably above 10^{-3} S/cm, and most preferably above 10^{-2} S/cm increases a battery's effectiveness.

The solubility of the sulfur species or conducting polymer in the electrolyte inhibits the efficiency of the battery. When sulfur species or other electroactive species associated with the conducting polymer are mobile in the electrolyte, the species may migrate towards the anode and a decrease in efficiency results when the species contact the anode. Over time the anode increasingly becomes contacted with species and a loss of electroactive sites may be seen on the anode. The solubility of the sulfur species also leads to collection of the active sulfur away from the conducting polymer and therefore a loss of redox species in the cathode. Thus, selecting sulfur species and conducting polymers which are not soluble in the electrolyte solution increases the efficiency of the battery and reduces the fade and poor cyclability typical of sulfur-based batteries.

The current sulfur-based batteries in use exhibit considerable fade over even 100 cycles. Many factors contribute to the fade observed in conventional sulfur-based batteries. However, by selecting the conducting polymer and sulfur species of the cathode materials

that are electrochemically stable to many repeated charge and discharge cycles the fade is reduced.

Unfortunately, previous sulfur-based cathodes have not satisfied most of these requirements. However, understanding the structure-function relationships for these materials allows sufficient tailoring of their properties to increase their effectiveness in rechargeable batteries.

Redox Mediation Window

In one embodiment, the selection of cathode materials is based on the overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials are chosen based on the redox mediation window. The conducting polymer mediates electrons between electrode and sulfur species.

An example of *inappropriate* overlap of thermodynamic potentials, the redox response of composite cathode components are shown in Figure 3. While oxidation of the organosulfur occurs when the polyaniline is primarily in its metallic state (indicated by a dashed line at 3.1 V), reduction of the resulting disulfide occurs in a potential window where the polyaniline is primarily in its insulating state (indicated by a dashed line at 2.6 V). The practical consequences of that thermodynamic mismatch between components is apparent in

devices using such cathodes – charging of the cells occurs quickly, but discharging is slow and typically incomplete.

Cathode Materials

Another aspect of the present invention pertains to resultant cathode materials identified by the use of the selection process of the present invention.

In a preferred embodiment, the cathode materials were selected because they exhibit overlap of the thermodynamic potentials of the electroactive constituents of the sulfur species and the conducting polymer. The cathode materials form a redox mediation window. The conducting polymer mediates electrons between electrode(s) and the sulfur species.

In a preferred embodiment, the resulting premise of the selection process of materials is the redox active species or sulfur species that are mobile are not compatible with long-life, high-capacity batteries. The sulfur species in the cathode materials is not mobile and is not soluble in the electrolyte of the battery and does not include labile protons that are mobile or soluble in the electrolyte. More preferentially, the cathode materials are not mobile. Specifically, the redox active species or sulfur species is not mobile. The redox active species is bound to the conducting polymer and is not able to migrate from the conducting polymer.

In a preferred embodiment, the cathode material is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer. The link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte. In this preferred embodiment, sulfur or other sulfur species in the cathode apart from the covalently linked sulfur species may or may not be present. Most preferably the cathode material contains no other sulfur or sulfur species apart from the bound sulfur species.

In a preferred embodiment, the cathode material is a thiophene based polymer (such as polythiophene) with covalently linked sulfur species. Such conducting polymers have been covalently-derivatized with sulfides and/or sulfide-containing groups as battery cathode materials. Physical constraints of the conducting polymer and sulfide components via covalent bonds which are present regardless of charge state of the cathode represents a novel step in the field.

Using the method of the present invention a resultant cathode material was identified. Sulfur-derivatized conducting polymers based on the oxide-substituted poly(thiophene) backbone are synthesized. Those polymers show good thermodynamic overlap with sulfide oxidation and reduction (*i.e.* charge and discharge). Covalent linkage of the sulfur groups to the backbone provides molecular-level ordering of the material, effecting homogeneous conductivity, cycling stability, and physical structure of the cathode.

In one embodiment, the sulfur-derivatized conducting polymers have the general formula $(R_i)_n(Y_jA_k)_m$ where R is monomer or oligomer units of a conducting polymer, i is 1 to n and n is greater than 20, more preferably greater than 100, more preferably greater than 1000, more preferably greater than 10,000 and most preferably greater than 100,000; Y is a functionalizing group that provides additional physical or chemical properties to the conducting polymer and j is 0 to n; A is a sulfur species, k is 1 to n and m is 1 to 12. A simplified representation of the general formula is shown in figure 3.

More particularly, the sulfur-derivatized conducting polymers have the general formula $(R)_n(YS_m)_x$ where R is a conducting polymer backbone and n is greater than 20, more preferably greater than 100, more preferably greater than 1000, more preferably greater than 10,000 and most preferably greater than 100,000; Y is a functionalizing group; S is an organosulfur moiety, m is 1 to 12 and x is 1 to 4. In a preferred embodiment, R is polythiophene or its derivatives. The formula is shown in figure 4. The preferred embodiment is shown in figure 5 based on the polythiophene backbone R_n .

Specifically, the present invention also concerns covalently derivatizing an electronically conducting polymer with a high density of electroactive sulfur species. The materials operate near the high oxidation potentials exhibited by the more common metal oxide cathodes but show far better ionic conductivity. This is accomplished by applying pre-existing, high yield organic synthesis procedures to the formation of monomeric, and then polymeric species composed of thiophene-based polymer chains with thiolate substituents. The synthesis steps are geared toward forming a reasonably high molecular weight polymer

while at the same time incorporating a high density of electroactive species that are not only electrochemically stable, but also protect the polymer from chemical degradation.

Another aspect of the present invention pertains to a method of designing conducting polymers covalently-derivatized with sulfur species such that the chemical, physical, and electrochemical properties of the designed material are advantageous to use in a rechargeable cell. For example, for the conducting polymers represented by Figure 6, the number of carbon atoms between the oxygen atoms and the sulfide-containing six-membered ring are varied to affect both the proximity of the sulfide-containing six-membered ring to the conducting polymer backbone and the flexibility of the attachment of the sulfide-containing six-membered ring. Likewise, other atom or functional groups such as sulfur, selenium, amides, amines, etc. are substituted for the oxygen atoms in order to affect the conductivity and relative energy of the conducting polymer backbone. Furthermore, the number of carbon atoms in the sulfide-containing six-membered ring are reduced or increased in order to affect the electronic, physical, or chemical properties of the sulfur atoms. For instance, reducing the number of carbon atoms to produce a sulfide-containing four-membered ring causes additional strain on the disulfide oxidation product and results in higher potentials for redox activity of that sulfur species. Finally, additional substituents are placed on the conducting polymer ring, functionalizing group, or sulfur species in order to affect the chemical and physical properties of the material. For instance, attaching a alkylsulfonate at the carbon atom above the oxygen atom increases the solubility and miscibility of the material.

Yet another aspect of the present invention pertains to a method of synthesis of the selected cathode material.

Still another aspect of the present invention pertains to batteries which comprise an anode; cathode material(s) of the present invention, as described herein; and a separator between the anode and the cathode materials. A battery with the cathode material as sulfur-derivatized conducting polymers based on the oxide-substituted poly(thiophene) backbone are used as a substitute cathode in existing lithium, lithium-ion, and lithium polymer rechargeable batteries.

Synthesis of Sulfur-Derivatized Cathode Materials.

Thiophene based cathode materials

Two thiophene-based polymers, structures shown in Figure 6, were synthesized. The first (PDDT) follows a tractable route to produce a material with an attractive theoretical specific capacity (235 A h/kg). Synthesis of the second polymer (PDPT) was more uncertain due to its bulky substituents, yet its synthesis yielded a material with a very attractive theoretical specific capacity (332 A h/kg).

PDDT was chosen as a cathode material in part because a stable 6-member ring is formed during oxidation to the disulfide.

PDPT, shown in Figure 6, offers higher specific capacity because of the increased number of disulfide substituents

Development of deposition techniques for the polymers synthesized

Processing of conducting polymers is a non-trivial issue – the very traits that make those materials conductive also result in low solubility of the polymers in most solvent systems. That problem is compounded for the systems described herein by the typically poor solubility of sulfide species.

For a preferred embodiment, if a particular polymer exhibits some solubility in a given, non-protic solvent such as N-methylpyrrolidinone or methylene chloride, then a saturated solution is directly cast onto the current collector. Care was taken to generate uniformly small particle sizes of the polymer prior to deposition. Evaporation of the solvent under normal drying conditions leads to a relatively adherent film due to the soluble phase acting as a binder. If a quality film is generated, but adhesion to the current collector is poor, then the current collector is chemically or mechanically treated prior to film deposition.

For another embodiment, mechanical or high pressure or temperature methods are employed to prepare suitable films of the cathode material. For example, extrusion, heat-pressing, and other methods are available.

In a preferred embodiment, the derivatized conducting polymer is prepared by chemical or electrochemical oxidation of its monomer in the presence of a suitable current collector. For example, the monomer of PDDT (Figure 6) is electrochemically oxidized at a stainless steel electrode by applying a potential of more than one volt versus the Ag/AgCl reference redox couple. This application results in the preparation of a film of PDDT on the stainless steel suitable for use as a cathode material.

If a particular polymer is not sufficiently soluble in any appropriate solvent system, and if the mechanical preparation of reasonable films is not possible, carbon paste electrodes containing the polymers are prepared in order to allow electrochemical testing of their properties.

Example 1

The first attempted, unsuccessful, synthesis involved Cu(I) assisted nucleophilic displacement of the bromine groups of 3,4-dibromothiophene with 1,2-dithiane-4,5-diol to form the desired cyclic ester (Scheme 1).

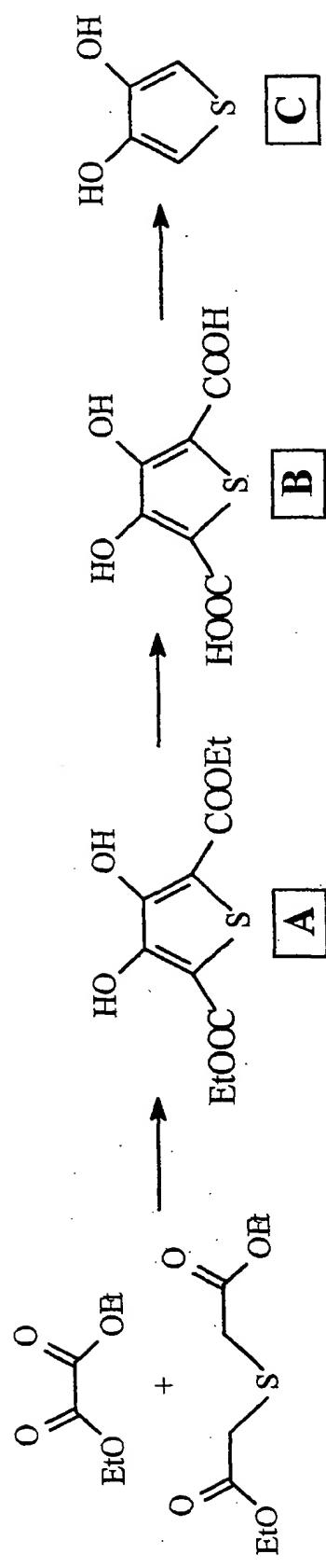
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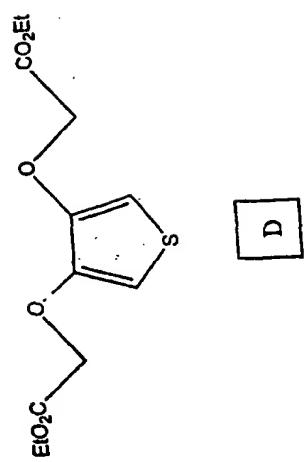
3,4-(1,2-dithiane-4,5-diol) Thiophene. Pyridine (5 mL) was added to 1,2-dithiane-4,5-diol (0.27 g, 1.80 mmol), CuI (0.01 g, 0.07 mmol) and KO^tBu (0.06 g, 0.54 mmol) to produce a yellow solution which turned green after stirring at ambient temperature over a period of 1h. 3,4-dibromothiophene (0.09 g, 0.36 mmol) was then added to the reaction mixture which was heated at 100 °C for 24h. A distillation was then done to remove pyridine. The remaining solution was dissolved in 0.05 M EDTA to remove complexed copper. An extraction was done with ethyl acetate. The organic, ethyl acetate, layer was concentrated under vacuum. This procedure did NOT result in the desired compound, the actual identity of the remaining solution was not confirmed.

At this point new synthetic procedure was devised (Scheme 2) utilizing 3,4-dihydroxythiophene. 3,4-dihydroxythiophene can be synthesized by adding 2,2'-thiobisacetate ethyl ester to diethyl oxalate in a solution of ethanol and sodium metal, according to the method of Hinsberg, to produce 3,4-dihydroxy-2,5-dicarbethoxythiophene, compound A in Scheme 3. Hydrolysis of compound A with ethanolic sodium hydroxide results in a dicarboxylic acid, compound B. Heating compound B under a reduced atmosphere causes sublimation of compound C as a yellow powder. Care must be taken in

Scheme 3

Route 1.





isolation because compound C decomposes readily on exposure to heat, light and moisture. Alternatively, a more direct approach toward the formation of 3,4-dihydroxythiophene is to add HS^- and a base, or simply S^{2-} , to 1,4-dibromo-2,3-butanedione. Once 3,4-dihydroxythiophene was obtained it was reacted with 2 equivalents of ethyl bromoacetate under basic conditions to form compound which when treated with 2 equivalents of LDA in the presence of I_2 or another oxidizing agent formed compound F. Alternatively, compound F can be synthesized by adding 3,4-dihydroxythiophene to a cyclic sulfate ethyl ester, compound E, in the presence of potassium tert-butoxide at elevated temperatures. Upon reduction of F with LiAlH_4 compound was formed. Treatment of G with PBr_3 resulted in the formation of compound H. Conversion of compound H to the desired monomer is accomplished by treatment with potassium thioacetate followed by acidification under aqueous conditions, then I_2 addition to result in the desired monomeric compound I. Alternatively, treatment of compound H with 2 equivalents of ammonium thiocyanate under acidic conditions in the presence of an oxidizing agent, I_2 , also resulted in formation of compound I. The same compound I was also formed by adding 2 equivalents of HS^- and an oxidizing agent to compound H. Polymerization of compound I was accomplished in the presence of FeCl_3 .

Experimental:

2,2'-thiobisacetate ethyl ester. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (14g, 58 mmol) was dissolved in an $\text{EtOH}/\text{H}_2\text{O}$ (60 mL/36 mL) solution. Ethyl bromoacetate was added. This was heated at 80 °C for 19 h under N_2 with an oil bath. Upon cooling to ambient temperature EtOH was removed *in vacuo* leaving a turbid aqueous solution. Washed with Et_2O (2 x 40 mL), dried the Et_2O layer with MgSO_4 . The Et_2O was evaporated under vacuum and the remaining solution was

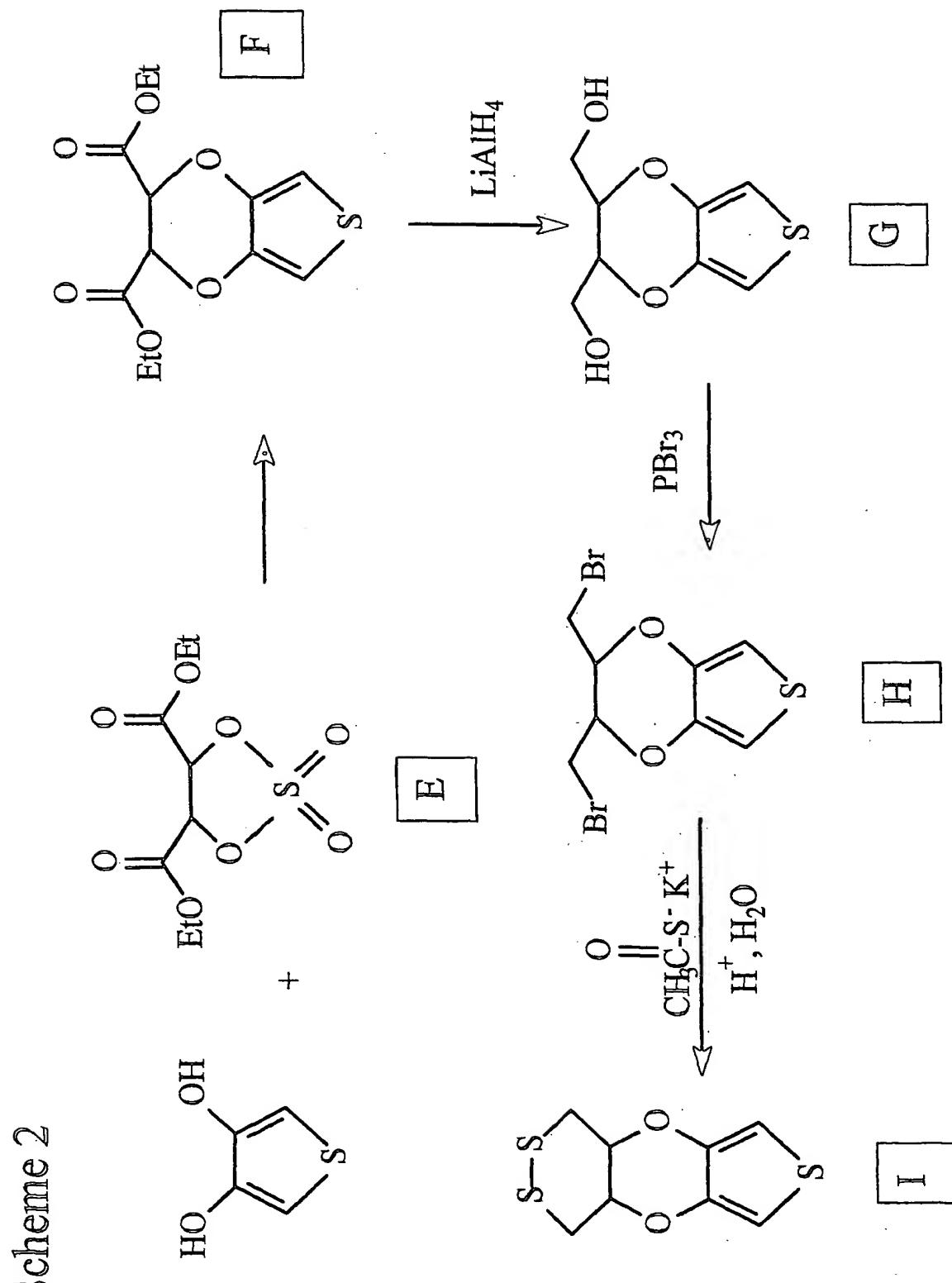
distilled to yield 4.66 g (39%) of a yellow oil. ^1H NMR (C_6d_6 , 400 MHz, 23 °C): δ 3.87 (q, 2H; OCH_2CH_3), 3.15 (s, 2H; SCH_2), 0.90 (t, 3H, OCH_2CH_3).

2,5-dicarbethoxy-3,4-dihydroxythiophene. Diethyl oxalate (6.58 g, 45 mmol) was added to 2,2' thiobisacetate ethyl ester (4.66 g, 23 mmol) to produce a yellow-orange solution. A solution of Na (1.56 g, 68 mmol) in EtOH (24 mL) was added to produce a white/yellow precipitate, this was mixed well for 10 minutes. H_2O (50 mL) was added to the reaction mass with cooling in an ice bath. Concentrated HCl was added dropwise until acidified. This was allowed to stand in the refrigerator for 12 days. At this point a cold filtration was done to isolate a white solid.

2,5-dicarboxy-3,4-dihydroxythiophene. EtOH (30 mL) was added to 2,5-dicarbethoxy-3,4-dihydroxythiophene (1 g). A solution of NaOH (4.0 g) in H_2O (20 mL) was added and refluxed under N_2 for 20 h. Upon cooling to ambient temperature the EtOH was removed by distillation and the residue was redissolved in H_2O then acidified with 15 % HClaq when a white ppt was obtained. This product was collected by filtration and washed with cold H_2O then crystallized from dilute MeOH to give colorless needles.

3,4-dihydroxythiophene. The acid, 2,5-dicarboxy-3,4-dihydroxythiophene (1g), was sublimed in a sublimation tube at 120 °C/3mm. The yellowish decarboxylated product was resublimed and then crystallized from benzene and ligroin to give pale yellow needles.

Cyclic sulfate ethyl ester. Carbon tetrachloride (25 mL) was added to diethyl-L-tartrate (4.3 mL, 25 mmol). Thionyl chloride (3.57 g, 30 mmol) was added via syringe slowly and the solution was refluxed for 50 min. then cooled in an ice bath and diluted with CH_3CN (25 mL). $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (8 mg, 0.03 mmol) and H_2O (38 mL) were added, followed by NaIO_4 (16 g, 75 mmol). The mixture was stirred at room temperature for 17 h. The mixture was then

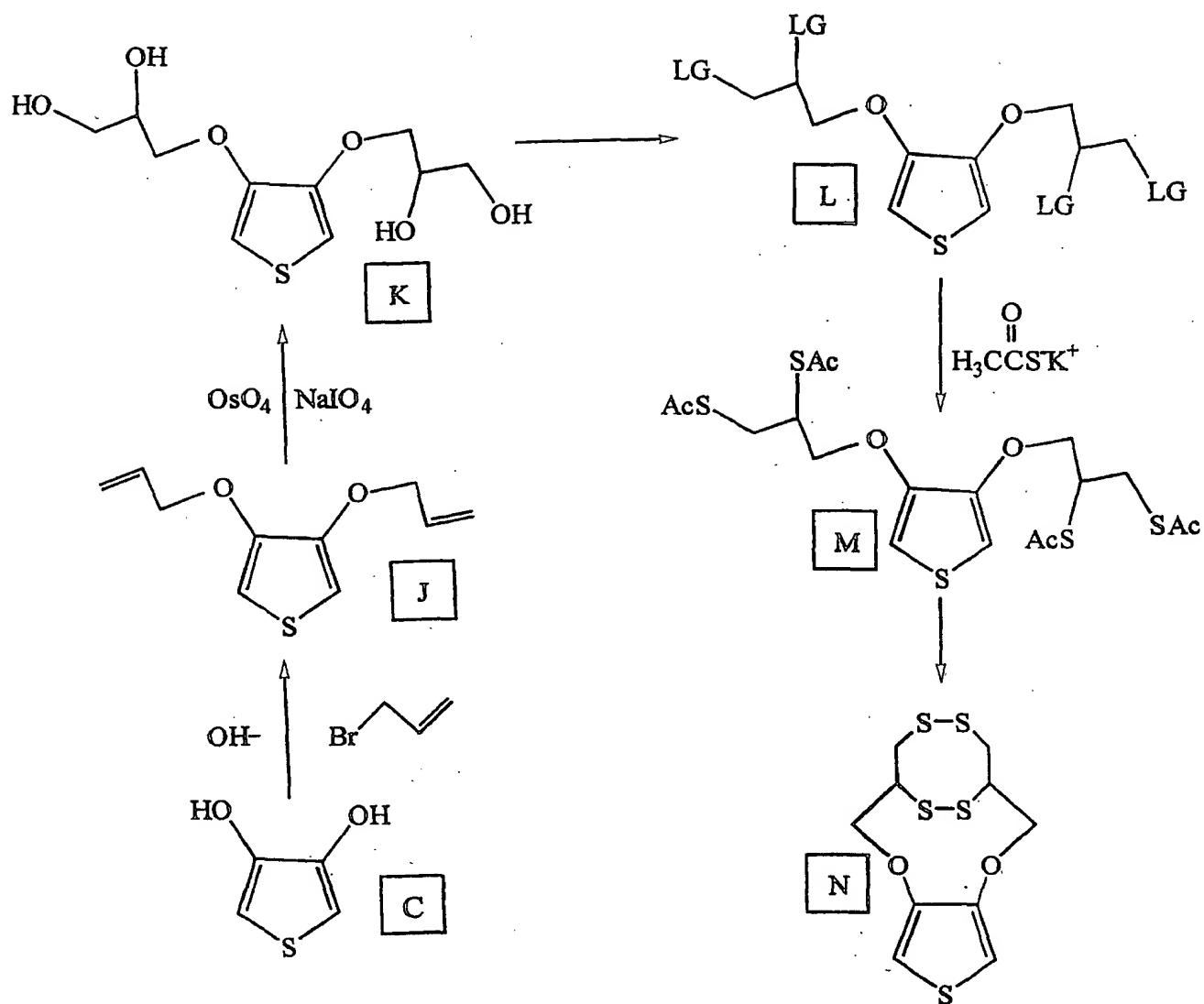


diluted with 200 mL Et₂O and the two phases were separated. The organic layer was washed with H₂O (10 mL), saturated NaHCO₃ (2 x 20 mL), and brine (10 mL). After drying over MgSO₄, the solution was filtered through a small pad of silica gel. The filtrate was then concentrated to yield analytically pure colorless crystals.

Example 3

The use of 3,4-dihydroxythiophene is also necessary in the synthesis of the second desired monomeric component shown in figure 2 and was synthesized as described above. Scheme 4 shows the mechanism of formation of the compound shown in figure 2. The reaction of 3,4-dihydroxythiophene with 2,2-dimethyl-1,3-dioxolane-4-metanol in the presence of a base, followed by H₃O⁺ addition, resulted in the formation of compound K. Alternatively, this is also formed by the addition of 2 equivalents of allyl bromide to 3,4-dihydroxythiophene in the presence of a base. The resulting product, J, was treated with catalytic amounts of OsO₄ and sodium periodate to produce compound K. Once compound K is obtained it was treated with PBr₃ or tosyl chloride to form L, where LG = Br or OTs. Compound L can also be produced by the addition of 1,2,3-tribromopropane to 3,4-dihydroxythiophene. Treatment of L with potassium thiolacetate resulted in formation of M. Polymerization of this material was done in the cathode assembly step followed by removal the thioacetate protecting groups during curing of the cathode, through the use of lithium hydroxide. Alternatively, compound N can be reached directly by treating compound L with HS- and an oxidizing agent. At this point polymerization of N was accomplished electrochemically.

Scheme 4



Experimental:

2,2'-thiobisacetate ethyl ester. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (14g, 58 mmol) was dissolved in an $\text{EtOH}/\text{H}_2\text{O}$ (60 mL/36 mL) solution. Ethyl bromoacetate was added. This was heated at 80 °C for 19 h under N_2 with an oil bath. Upon cooling to ambient temperature EtOH was removed *in vacuo* leaving a turbid aqueous solution. Washed with Et_2O (2 x 40 mL), dried the Et_2O layer with MgSO_4 . The Et_2O was evaporated under vacuum and the remaining solution was distilled to yield 4.66 g (39%) of a yellow oil. ^1H NMR (C_6d_6 , 400 MHz, 23 °C): δ 3.87 (q, 2H; OCH_2CH_3), 3.15 (s, 2H; SCH_2), 0.90 (t, 3H, OCH_2CH_3).

2,5-dicarbethoxy-3,4-dihydroxythiophene. Diethyl oxalate (6.58 g, 45 mmol) was added to 2,2'-thiobisacetate ethyl ester (4.66 g, 23 mmol) to produce a yellow-orange solution. A solution of Na (1.56 g, 68 mmol) in EtOH (24 mL) was added to produce a white/yellow precipitate, this was mixed well for 10 minutes. H_2O (50 mL) was added to the reaction mass with cooling in an ice bath. Concentrated HCl was added dropwise until acidified. This was allowed to stand in the refrigerator for 12 days. At this point a cold filtration was done to isolate a white solid.

2,5-dicarboxy-3,4-dihydroxythiophene. EtOH (30 mL) was added to 2,5-dicarbethoxy-3,4-dihydroxythiophene (1 g). A solution of NaOH (4.0 g) in H_2O (20 mL) was added and refluxed under N_2 for 20 h. Upon cooling to ambient temperature the EtOH was removed by distillation and the residue was redissolved in H_2O then acidified with 15 % HClaq when a white precipitate was obtained. This product was collected by filtration and washed with cold H_2O then crystallized from dilute MeOH to give colorless needles.

3,4-dihydroxythiophene. The acid, 2,5-dicarboxy-3,4-dihydroxythiophene (1g), was sublimed in a sublimation tube at 120 °C/3mm. The yellowish decarboxylated product was resublimed and then crystallized from benzene and ligroin to give pale yellow needles.

CLAIMS

- 1) A method of selecting cathode materials for a sulfur-based Lithium battery wherein the cathode comprises a conducting polymer and a sulfur species;
identifying a characteristic of the conducting polymer;
identifying a characteristic of the sulfur species;
evaluating the characteristic of the conducting polymer and the sulfur species;
selecting the conducting polymer and the sulfur species based on the identified characteristic;
wherein the identified characteristic of the sulfur species and the identified characteristic of the conducting polymer are at least one characteristic selected from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; a high density of electroactive species per weight and volume/large inherent charge capacity $> 230 \text{ Ah/kg}$; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer; reasonable electronic conductivity (10^4 S/cm) of the cathode materials; no solubility in electrolyte solutions; or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.
- 2) The method of claim 1 wherein the identified characteristics are all of the at least one characteristics.

3) The method of claim 1 wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer.

4) The method of claim 1 wherein the at least one characteristic is no solubility in electrolyte solutions.

5) A cathode material for use in a sulfur-based Lithium battery comprising a sulfur species and a conducting polymer;
wherein the conducting polymer and the sulfur species exhibit at least one characteristic selected from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; a high density of electroactive species per weight and volume/large inherent charge capacity $> 230 \text{ Ah/kg}$; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer; reasonable electronic conductivity (10^{-4} S/cm) of the cathode materials; no solubility in electrolyte solutions; or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.

6) The cathode material of claim 5, wherein the at least one characteristic includes all of the characteristics from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for Li^+ ions; a high density of electroactive species per weight and volume/large inherent charge capacity $> 230 \text{ Ah/kg}$; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

reasonable electronic conductivity (10^{-4} S/cm) of the cathode materials; no solubility in electrolyte solutions; or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.

- 7) The cathode material of claim 5, wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer.
- 8) The cathode material of claim 5, wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer and no solubility in electrolyte solutions.
- 9) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species and a conducting polymer wherein the conducting polymer is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer.
- 10) The cathode material of claim 9, wherein the covalent link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte.
- 11) The cathode material of claim 9, wherein the electrolyte contains no other sulfur or other sulfur species except for the linked sulfur species.

12) The cathode material of claim 9, wherein the cathode material is a thiophene based polymer with the covalently linked sulfur species.

13) The cathode material of claim 9, wherein the conducting polymer are covalently-derivatized with sulfides and/or sulfide-containing groups.

14) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species including sulfide components and a conducting polymer wherein the conducting polymer is a single component sulfur-based conducting polymer wherein physical constraints of the conducting polymer and the sulfide components via covalent bonds which are present regardless of charge state of the cathode material.

15) An electric current producing cell comprising:

- a) an anode;
- b) a cathode containing a cathode material of claim 14; and,
- c) an electrolyte between the anode and cathode.

16) An electric current producing cell comprising:

- a) an anode;
- b) a cathode containing a cathode material of claim 12; and,
- c) an electrolyte between the anode and cathode.

17) An electric current producing cell comprising:

- a) an anode;
- b) a cathode containing a cathode material selected by the method of claim 2; and,
- c) an electrolyte between the anode and cathode.

18) The cathode material of claim 13, wherein the sulfur-derivatized conducting polymer is represented by a formula $(R_i)_n(Y_jA_k)_m$ (where R is monomer or oligomer units of the conducting polymer, i is 1 to n and n is greater than 20, Y is a functionalizing group that provides additional physical or chemical properties to the conducting polymer and j is 0 to n; A is the sulfur species, k is 1 to n and m is 1 to 12.

19) The cathode material of claim 18, wherein n is greater than 1000.

20) The cathode material of claim 19, wherein n is greater than 100,000.

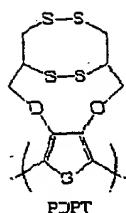
21) The cathode material of claim 13, wherein the sulfur-derivatized conducting polymer is represented by a formula $(R)_n(YS_m)_x$ (where R is a conducting polymer backbone and n is greater than 20; Y is a functionalizing group; S is an organosulfur moiety, m is 1 to 12 and x is 1 to 4.

22) The cathode material of claim 21, wherein n is greater than 1000.

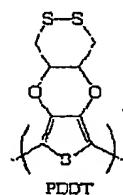
23) The cathode material of claim 22, wherein n is greater than 100,000.

24) The cathode material of claim 21, wherein R is polythiophene or its derivatives.

25) The cathode material of claim 24, wherein the single component sulfur-based conducting polymer is represented by:



26) The cathode material of claim 24, wherein the single component sulfur-based conducting polymer is represented by:



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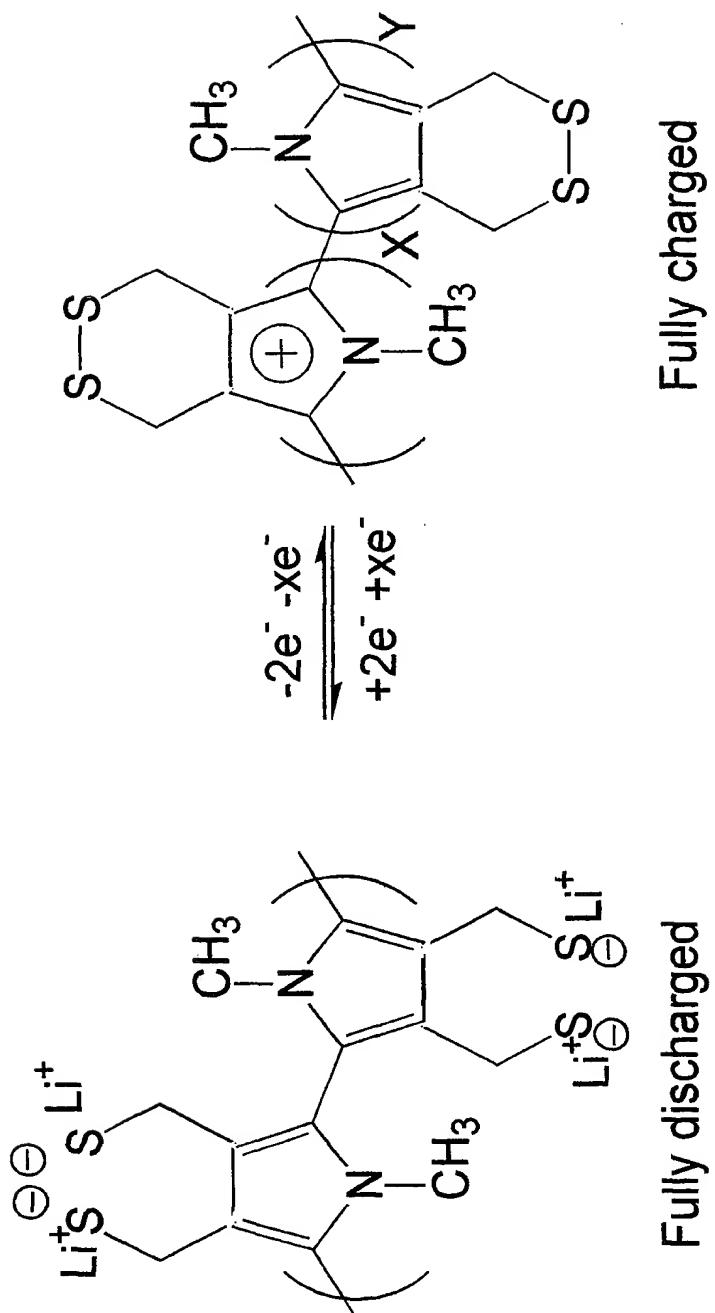


Fig. 1

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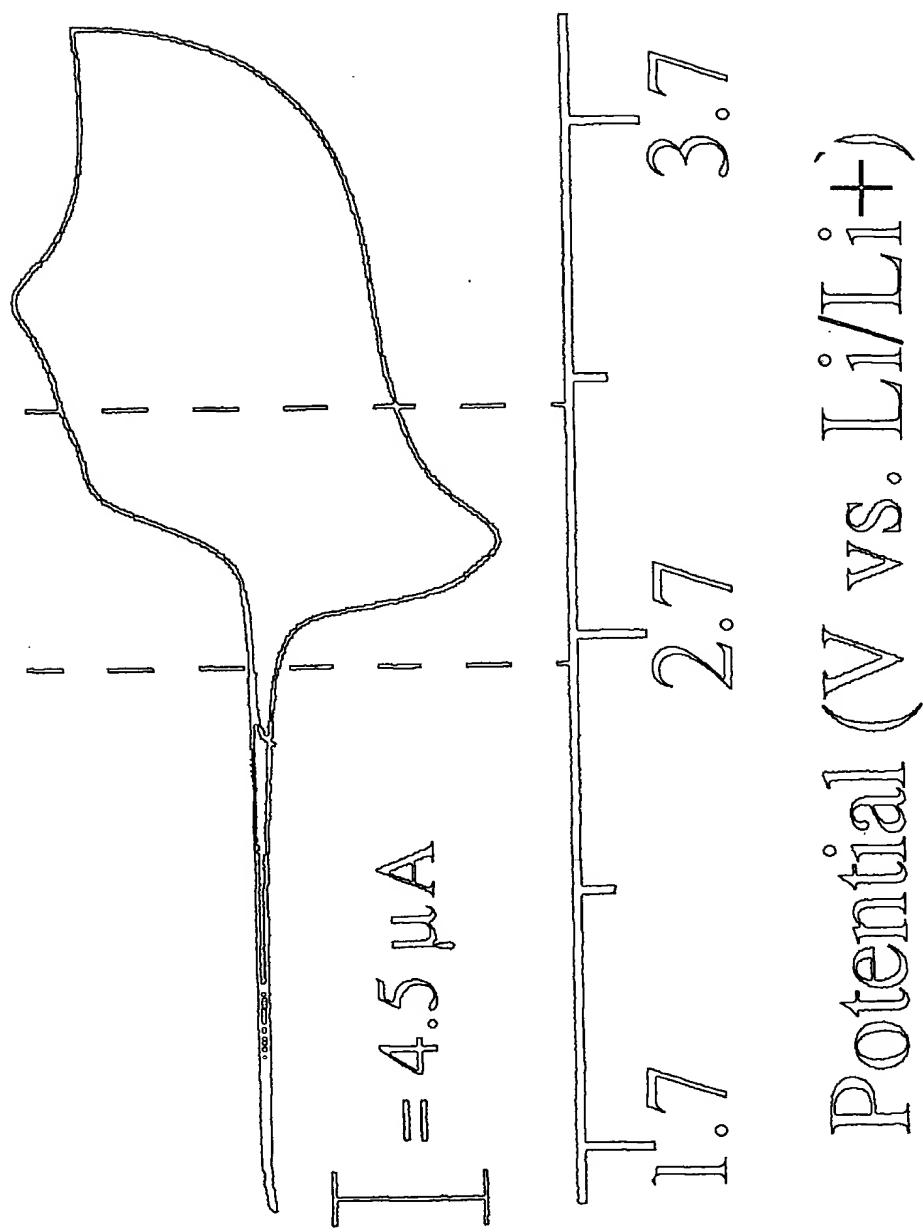


Fig 2

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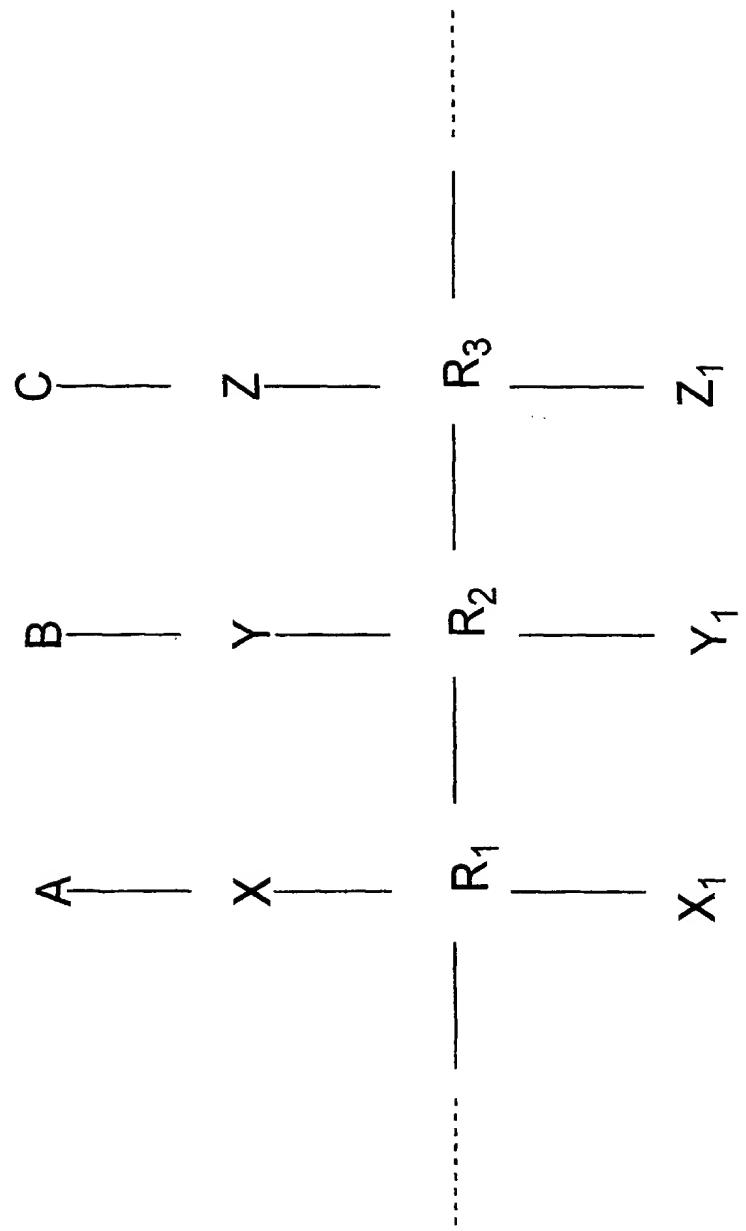


Fig. 3

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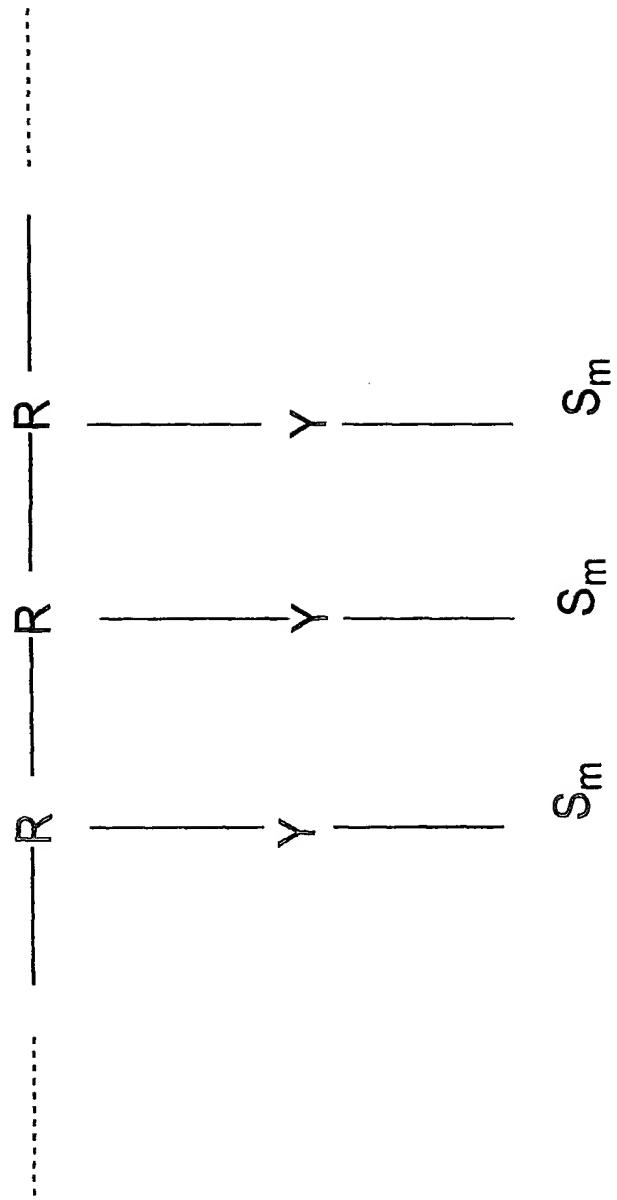


Fig. 4

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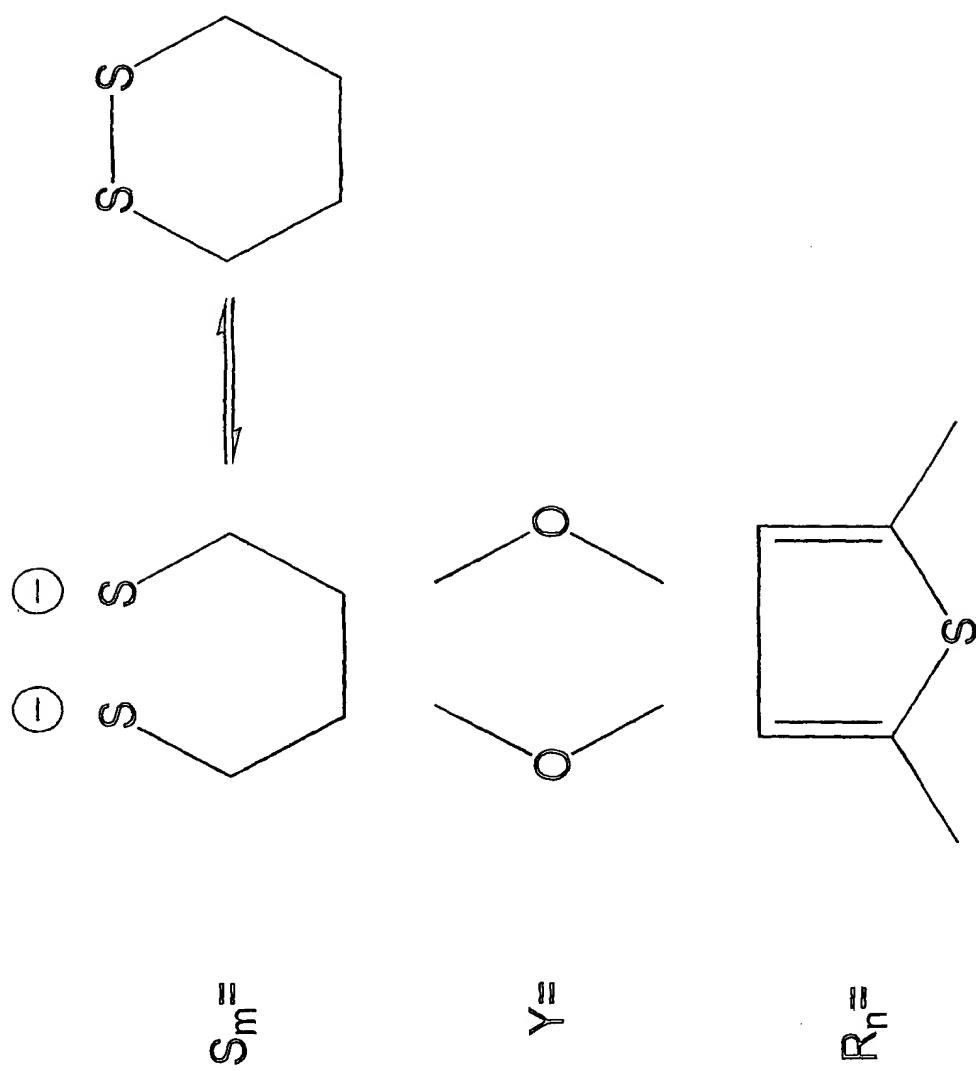
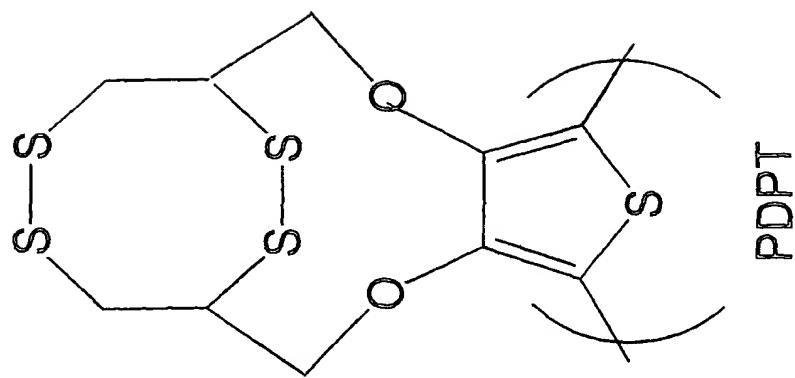
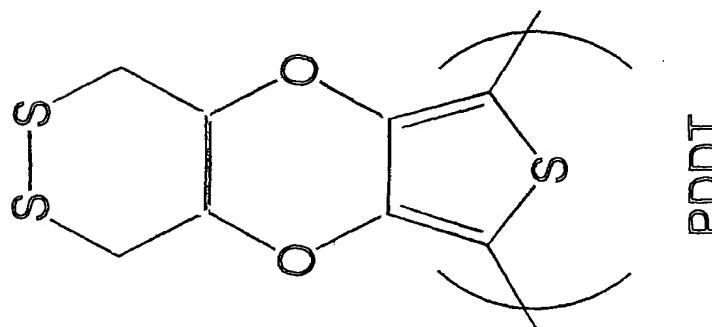


Fig. 5

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PDPT



PDDT

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/02445

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01M 4/60

US CL :429/213

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/213

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST, Non-Patent Literature (Elsevier Science Search)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,472,488 A (MAXFIELD et al.) 18 September 1984, col. 4, lines 47-54.	9-24
X	US 5,723,230 A (NAOI et al.) 03 March 1998, col. 10, lines 16-36.	9-23
X	US 5,712,057 A (FAUTEUX) 27 January 1998, col. 2, lines 47-56.	9-23
A	US 4,869,979 A (OHTANI et al.) 26 September 1989, the entire document.	9-26

Further documents are listed in the continuation of Box C.

See patent family annex.

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
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Date of the actual completion of the international search

02 JUNE 2000

Date of mailing of the international search report

15 JUN 2000

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